SCHOOL OF CIVIL ENGINEERING

JOINT HIGHWAY RESEARCH PROJECT

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ANALYSIS OF HARDENED CONCRETE FOR ADMIXTURE CONTENT

L. C. Muszynski

PURDUE UNIVERSITY
INDIANA STATE HIGHWAY COMMISSION

Interim Report

ANALYSIS OF HARDENED CONCRETE FOR ADMIXTURE CONTENT

TO: H. L. Michael, Director
Joint Highway Research Project

February 8, 1979

Project: C-36-65D

FROM: W. L. Dolch, Research Associate
Joint Highway Research Project

File: 5-15-4

Attached is an Interim Report on the HPR Part II research study titled "Analysis of Hardened Concrete for Admixture Content". The Report also has that title and has been authored by Mr. Larry C. Muszynski, Graduate Instructor in Research on our staff. Professor W. L. Dolch of our staff directed the Study.

The purpose of the research is to develop a general analytical technique for the qualitative determination of the most common organic admixtures used in concrete. The work performed and reported herein concludes that organic admixtures can be extracted from hardened cementitious materials and by developed techniques can be identified. Work is continuing on quantifying the identification characteristics of various admixtures so that specific admixture content can be determined. This will be included in the Final Report to be submitted late in FY 79.

The Report after presentation to the JHRP Board will be forwarded to ISHC and FHWA for their review, comment and acceptance as partial fulfillment of the objectives of the Study.

Respectfully submitted,

W. L. Dolch

W. L. Dolch
Research Associate

WLD:ms

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Interim Report

ANALYSIS OF HARDENED CONCRETE FOR ADMIXTURE CONTENT

by

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Graduate Instructor in Research

Joint Highway Research Project

Project No.: C-36-65D

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16. Abstract

Twenty concrete admixtures, including air-entraining agents, water reducing retarders, accelerators, and super plasticizers, were added, both alone and in common combinations, to cement pastes in amounts typically used in concrete practice. The hardened and cured pastes were crushed, and the organic constituents were extracted from the No. 4 - No. 16 fraction in a Soxhlet apparatus. Various extraction solvents were tried, and the one selected as best was a ternary azeotrope of 75 percent methlethyl ketone, 14 percent ethanol, and 11 percent water by volume. The extracts were evaporated to dryness and then dissolved in a carrier phase and subjected to high pressure liquid chromatography using both ultraviolet absorbance and refractive index detectors. A variety of carrier solvents, column packings, and types of chromatographic operations were tried before suitable conditions for separation and identification of these materials were found. The carrier solvent selected was 80 percent acetonitrile and 20 percent water by volume. The column packing selected as a micro - C_{18} material in reverse phase operation. The recorded ultraviolet detector output was found to give patterns that were unique for the admixture or admixture combinations used, so that identification of the materials is possible with this technique. Because the results are influenced by instrumental and technique variables, cement paste standards containing the admixture(s) under test should be used.

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Figures 1 through 4 and 6 through 12 are used courtesy of Waters Associates.

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HIGHLIGHT SUMMARY

Twenty concrete admixtures, including air-entraining agents, water reducing retarders, accelerators, and super plasticizers, were added, both alone and in common combinations, to cement pastes in amounts typically used in concrete practice. The hardened and cured pastes were crushed, and the organic constituents were extracted from the No. 4 - No. 16 fraction in a Soxhlet apparatus. Various extraction solvents were tried, and the one selected as best was a ternary azeotrope of 75 percent methlethyl ketone, 14 percent ethanol, and 11 percent water by volume. The extracts were evaporated to dryness and then dissolved in a carrier phase and subjected to high pressure liquid chromatography using both ultraviolet absorbance and refractive index detectors. A variety of carrier solvents, column packings, and types of chromatographic operations were tried before suitable conditions for separation and identification of these materials were found. The carrier solvent selected was 80 percent acetonitrile and 20 percent water by volume. The column packing selected was a micro - C_{18} material in reverse phase operation. The recorded ultraviolet detector output was found to give patterns that were unique for the admixture or admixture combinations used, so that identification of

the materials is possible with this technique. Because the results are influenced by instrumental and technique variables, cement paste standards containing the admixture(s) under test should be used.

CHAPTER I - INTRODUCTION

The use of organic admixtures, such as water-reducing, set-retarding, and air-entraining agents that alter the properties of portland cement concrete, has become common practice in the concrete industry (1). The number and variety of marketed admixtures is large, and combinations of these admixtures in the concrete complicates analysis of the concrete for the presence of these substances.

Concrete that has proved unsatisfactory, either from a strength or durability point of view, is frequently questioned as to whether it had added to it the amount of admixture called for in the specifications. Any method for the analysis, qualitative or quantitative, of organic admixtures in concrete is complicated by several considerations. The admixture is present in small quantities. A typical value is 0.1 percent of the amount of cement. The organic substance in question may have reacted in the highly alkaline environment with constituents of the cement. There may be interference from other substances present, e.g. grinding aids in the cement or other admixtures in the concrete. Also, admixture formulations may be changed by their producers from time to time without any public knowledge of the change.

Present methods of analyzing hardened concrete for these components leave much to be desired. The methods are tedious, relatively inaccurate, and in some cases depend upon considerable intuitive insight and

experience lacking in most analysts who may be called upon to perform the tests.

The purpose of this work was to develop a general analytical technique for the qualitative determination of the most common organic admixture used in concrete. The technique chosen for exploration was high-pressure liquid chromatrography, which seemed to offer promise as a general method. It was, therefore, necessary first to develop an efficient way of extracting the organic material from the hardened concrete, and secondly to devise an analytical scheme of separating and identifying the materials in question.

CHAPTER II - REVIEW OF LITERATURE

High Pressure Liquid Chromatography

A brief review will first be given of the various modes in which the high pressure liquid chromatography technique is operated. A general text is that of Snyder and Kirkland (2).

Liquid chromatography is used to separate chemical mixtures into their individual components. A dilute solution of the sample is passed through a column packed with solid particles. With the proper solvent, operating conditions, and column packing material, some components in the sample will travel through the column more slowly than others, thus forming the basis for a liquid chromatographic separation.

Pumping the solution through a column at relatively high pressures (100-3000 psi), and using small particles for column packing material, forms the basis for high speed liquid chromatography or high pressure liquid chromatography (HPLC). This variant increases the speed of separation. The use of small packing particles (5-20 um) in the column reduces the diffusion paths in the retardant bed and produces an increase in the number of components that can be separated at a given carrier strength (composition of mobile phase).

The materials selectively eluted as further solvent passes down the column are detected and their presence and amount is recorded in some suitable manner.

The two most widely used detector systems for a high pressure liquid chromatograph are a differential refractometer and an ultraviolet absorbance spectrograph. The differential refractometer monitors change in refractive index produced by the components eluted from the column in reference to the refractive index of the pure solvent. The ultraviolet absorbance detector measures the absorbance, at some given wavelength of radiation, of the solution leaving the column. This detector is obviously specific for compounds that absorb the given ultraviolet radiation, but is much more sensitive than the refractive index detector. The use of both detectors more than doubles the output of information contained in a chromatogram, since the interrelationships between the refractive index peaks and the ultraviolet absorbance peaks are invaluable for diagnostic work.

In either case, the output is a peak or peaks on a recorder chart. Ideally, these peaks will form a basic pattern or fingerprint that is unique among those of the other admixtures, resulting in an analytical separation that is qualitative. The peak height or its area is proportional to the amount of substance giving rise to the peak; therefore, the analytical separation technique is also semi-quantitative.

High pressure liquid chromatography operates in four basic modes: liquid/solid (adsorption), liquid/liquid (partition), ion-exchange and gel permeation. The broad utility of this technique is a consequence of the fact that a sample can be analyzed by at least one, if not more, of these procedures.

Liquid/solid separation is performed with a liquid mobile phase and a stationary solid surface which reversibly adsorbs the solutes. The

mobile phase is usually a relatively non-polar solvent used in conjunction with a polar solid packing, e.g. silica gel; this is referred to as normal phase liquid/solid chromatography. When a non-polar packing, such as a high polymer, is used with a polar mobile phase it thus becomes reverse phase liquid/solid chromatography.

In liquid/liquid chromatography, the stationary solid surface is coated with a second liquid (the stationary phase) which is immiscible in the mobile liquid phase. The relative distribution or partition of the sample components between the mobile phase and the stationary phase determines how much separation occurs. A polar stationary phase in combination with a non-polar mobile phase is termed normal phase liquid/liquid chromatography. If the stationary phase is non-polar, such as a hydrocarbon, and a polar mobile phase is used, such as water, the technique is termed reverse phase liquid/liquid chromatography.

Although this technique is the most versatile, it is not without some experimental difficulties. In this mode of chromatography, separation depends upon two mutually insoluble liquid phases that are saturated with respect to each other. Since most liquids are not totally insoluble in one another, the mobile phase gradually strips away the stationary phase that was coated onto the support. Due to this solubility problem, column packings have been developed, in which the stationary phase is permanently bound to the support by chemical bonding. These packings are called bonded phase packings, and they are used in the reverse phase mode, i.e. polar mobile phase.

Ion exchange separations are made between a polar mobile phase, usually water, and a stationary ion exchange resin with either acidic

or basic counter ion. The separation depends upon the ionic nature of the solutes and their relative affinity for the ion exchange surface. Ion-exchange materials usually consist of high molecular weight polymers to which ionic groups are chemically bonded. The cation exchangers contain either sulfonic acid (strong cationic) or carboxylic acid (weak cationic) groups. The anion exchangers have quaternary amine (strong anionic) or primary amine (weak anionic) groups.

Since this type of separation is dependent upon the sample being in its ionic form, the pH of the eluent has a large effect on the ionic nature of weak acids and bases. If the pH of the eluent is equal to the pKa of the acid or base, then the sample will be only 50% in the ionic form. Therefore small changes in pH and ionic strength have a significant effect on the separation, since only the ionic form of the sample is bound to the ion-exchange packing. Ion exchange packings have certain limitations, very low exchange capacity for very small particles, low stability and questionable reproduceability.

Two techniques that function in the ion-exchange mode yet have the advantages of reverse phase liquid/liquid partition using bonded phase packings are called Paired-Ion Chromatography (PIC) and Ion-Suppression Chromatography (ISC).

Weakly ionic compounds, acids and bases, those with pKa's greater than 2 and less than 8, can be separated by Ion-Suppression reverse phase chromatography. The polar mobile phase is buffered to drive the equilibrium to the left.

$$\text{Non-Ionic} \rightleftharpoons \text{ionic}$$

Thus keeping the sample in the less polar, non-ionic form, which can be retained on the non-polar bonded phase packing.

Strong acids and bases, that are in the ionic form at most normal pH values, can be analyzed by reverse phase chromatography when an appropriate counter-ion is added to the eluent. The large organic counter-ions form an equilibrium complex with the ionic sample, which results in a species that can be separated on non-polar bonded phase packings. This technique is referred to as paired-ion chromatography (PIC), (3,4,5). For basic samples, alkyl sulfonates are used as counter-ions, and quaternary amines for acidic samples. Variables in paired-ion chromatography include pH, type and concentration of counter-ion, and type of stationary phase (bonded phase).

Another form of this ion-pairing technique, called "soap chromatography" (6) employs a detergent, e.g. cetyltrimethylammonium bromide, as the counter-ion. The difference appears to be that the "soap" counter-ion forms a more highly stable ion-pair with the sample that will not dissociate in the presence of strongly hydrogen-bonding surface groups.

Gel-permeation chromatography is a mechanical sorting of molecules based on the size of the molecules in solution. Size separation is achieved with a porous packing gel which is compatible with the mobile phase. The packing material behaves like a sieve. It allows the smallest molecules to enter the packing pores and excludes the larger molecules. The small molecules have a longer path to travel through the length of the column, due to their diffusion in and out of the pores of the packing material. The larger molecules pass quickly through the column since their diffusion path is shorter. The chromatographic

separation is thus one of size, the larger molecules exiting first and the smaller molecules later. Since the size of the molecules is related to its molecular weight, the time of elution gives an approximation of its molecular weight. In true gel-permeation chromatography the components of the sample should not have any affinity for the packing.

Analysis of Admixtures in Concrete

Relatively few methods for the determination of organic admixtures in hardened concrete have been published. Admixtures used in concrete are described in ACI 212 (7). The small amount of work prior to 1966 (8-13) was reviewed by Hime et al (14). These methods were generally limited to one compound or class of compounds, and those for lignosulfonates are the only ones in relatively wide use.

Hime (14) proposed a general scheme. It was based on three extraction procedures--a chloroform extraction, an acid decomposition followed by a chloroform extraction, and an extraction with a sodium carbonate solution, which is specific for lignosulfonates. The extracted substances are then identified by infrared spectrophotometry. Halstead and Chaiken (15) had earlier published infrared spectra for some of these materials. The infrared methods have the advantage of generality and, in favorable cases, can be semi-quantitative. If more than one material is present the interpretation of the spectrum is difficult, and in general, the correct assessment of the spectrum depends upon a degree of experience with the method that is rare.

Determination of lignosulfonates have been the subject of the most attention. Several methods include aqueous extraction and subsequent oxidation of the extracted lignin-like material to vanillin; the vanillin

is then measured colorimetrically (16), aqueous sodium carbonate extraction followed by ultraviolet spectrophotometry (12, 14, 17), acid decomposition and removal of ferric ions followed by ultraviolet spectrophotometry (18, 19).

Other attempts to determine admixtures include a colorimetric determination of polyhydroxy organic acids such as gluconates (20), the Wexler acetate method for acetate compounds using gas chromatography (21), and oxidation of alkanolamines and subsequent Nesslerization and colorimetry for determination of concentration (22,23). These methods have been reviewed by Dodson (17).

Methods of chemical analysis of air-entraining admixtures have not received as much attention as those for water-reducing retarding admixtures. Halstead and Chaiken (24) describe a scheme of identifying and controlling the uniformity of various air-entraining admixtures used in concrete. Vinsol resin has been determined by acid decomposition, chloroform extraction, and analysis of the methoxy content (9, 25); Darex is determined by a method that utilizes an oxidizing agent and Nesslerization, followed by colorimetric analysis (22, 23). These methods have proved tedious and complex. Sometimes other admixtures or additions containing amines would also be oxidized and yield erroneous results.

Recently, interest has been directed toward analyzing cement pastes and concrete for triethanolamine. McCall and Mannone (26), using gas chromatographic analysis, concluded that triethanolamine could not be efficiently extracted from cement pastes after more than a few hours of hydration. They also used the aqueous sodium carbonate extraction

technique followed by chloroform extraction and infrared analysis. The infrared spectrum obtained was not the spectrum expected if the triethanolamine was completely recovered. Connolly and Hime (27) developed a method for the analysis of triethanolamine in cement paste, mortar, and concrete. Their method consists of extracting the sample with hot water, followed by an ethanol extraction, converting the amine residue to its hydrochloride salt, and its analysis by infrared spectrophotometry. The infrared spectrum of treated extracts from concrete doped with triethanolamine clearly shows that triethanolamine can be detected in concrete samples. The technique is sensitive for qualitative detection of triethanolamine. However, the accuracy of their method did not consider the amount of triethanolamine recovered. Jawed and McCall (28) used the Connolly and Hime method of extraction and quantified the infrared analysis by using an internal standard. They determined that the percent of triethanolamine recovered was a function of the initial concentration of the triethanolamine added to the pastes. The recovery varied in such a way that, as the initial concentration of triethanolamine decreased, the percent recovery decreased. At an initial concentration of 0.5 percent, approximately 83 percent of the triethanolamine was recovered, and at an initial concentration of 0.005 percent, approximately 11 percent of the triethanolamine was recovered.

G. Fallick and J. Waters (29) reviewed one of the possible uses of high pressure liquid chromatography:

> "to identify the major components in wood chemicals and their derivatives".

They also claimed:

"all that is required is for the sample to be dissolved in a suitable solvent".

Since many of the admixtures used in concrete are derivatives of the process used in the manufacture of paper pulp, HPLC appeared to be a potentially good way to separate, characterize, and identify the chemical admixtures.

Broker and Simatupang (30) investigated "the chemical characterization of substances that disturb the hardening of cement" by thin layer chromatography. Sugars and lignosulfonic acids were extracted from different types of wood and characterized using this technique. Some limitations apparent in thin layer chromatography are longer separation times, difficult quantitation and poor reproduceability (2).

Simatupang (31) later used gel-permeation chromatography to characterize cement admixtures. He determined an average molecular weight for a lignosulfonate admixture as about 7500, using 0.1N acetic acid as the mobile phase and Sephadex-25 as the stationary phase, while continuously monitoring the UV absorption at 280 nm. The eluent was also analyzed for sugar content by the orcinol-sulfuric acid colorimetric test. The chromatograms obtained indicated different molecular weight distribution for the various admixtures analyzed.

CHAPTER III - MATERIALS AND EQUIPMENT

Admixtures

There were twenty admixtures used in the work, nineteen of which were proprietary and one was a pure chemical compound. The proprietary materials were obtained as samples from the producers. There were three air-entraining agents, four super-plasticizers, and twelve admixtures classifiable under ASTM C 494. The reagent material was triethanolamine. The code numbers assigned to these materials and some information about them are given in Table 1.

Cement

The cement used was an ASTM Type I, Lab. No. 323, the properties of which are shown in Table 2.

Water

Deionized water was used for all experiments, including sample preparation, Soxhlet extraction solvent, and part of the mobile phase.

Reagents

Technical grade methyl ethyl ketone (MEK), absolute ethanol (EtOH), and deionized water (H_2O) were used in preparing the extraction solvent. Reagent grade acetonitrile, and deionized water were used in preparing the mobile phase. The 80 percent acetonitrile - 20 percent water composition was filtered and deaired prior to its use as the mobile phase.

Table 1 - List of Admixtures

Code Letter	ASTM Designation	Chemical Description	Normal Dosage Rate (fl. oz./100# of cement)
A	*	Neutralized Vinsol Resin	0.5 - 1.5
B	A	Polymer	3 - 5
C	D	Salt of Hydroxy Carboxylic Acid	2 - 4
D	*	Sulfonated Hydrocarbon + TEA @	0.75 - 3
E	A	Calcium Lignosulfonate + TEA	7
F	A	Calcium Lignosulfonate + TEA + a Saccaride	3
G	D	Calcium Lignosulfonate	6 - 12
H	D	Salt of Gluconic Acid	2 - 4
I	D	Calcium Lignosulfonate + a Saccaride	2 - 4
J	C	Calcium Formate	0.5 - 2.0 #/100# cement
K	*	Neutralized Vinsol Resin	0.25 - 1.5
L	A	Multicomponent Polymer Product	3 - 5

Type A - Water-Reducing Admixture, ASTM C-494
Type B - Set-Retarding Admixture, ASTM C-494
Type C - Set-Accelerating Admixture, ASTM C-494
Type D - Water-Reducing and Set-Retarding Admixture, ASTM C-494
* - Air-entraining Agent, meets ASTM C-260 Specifications
@ - TEA - Triethanolamine

Table 1, (cont'd)

Code Letter	ASTM Designation	Chemical Description	Normal Dosage Rate (fl.oz/100# of cement)
M	B	Multicomponent Polymer Product	3-5
N	C	Multicomponent Product ($CaCl_2$)	16-32
O	D	Salt of Hydroxy Carboxylic Acid	1.5-3
P	**	Polymer of a Salt or Naphthalene Sulfonic Acid condensed with Formaldehyde	0.8-1.2% by wt. of cement
Q	**	Polymer of a Salt of Melamine Sulfonic Acid condensed with Formaldehyde	20
R	**	Same as P	32 (of a 1-3% soln.)
S	**	Similar to P	1.5% by wt. of cement
T	--	Triethanolamine	0.005-0.5% by wt. of cement
Control	--	No Admixture Added	--

** - Super Water-Reducing Admixture

Table 2 - Composition and Properties of Lab Cement No. 323

Chemical Analysis

	(%)
SiO_2	21.33
Al_2O_3	4.96
Fe_2O_3	2.44
CaO	64.71
M_9O	1.14
SO_3	3.32
Na_2O	0.07
K_2O	0.72
Loss on Ignition	1.18
Total	99.87
Insoluble Residue	0.33

Compound Composition

	(%)
C_3S	55.05
C_2S	19.62
C_3A	9.02
C_4AF	7.42
$CaSO_4$	5.64
Total	96.75

Physical Tests

Fineness:

325, % Passing	86.3
Wagner, $cm^2/9$	1820
Blaine, $cm^2/9$	3610

Compressive Strength (ASTM C-109):

1 - day	2095 (psi)
3 - day	3650 (psi)
7 - day	4550 (psi)
28 - day	5780 (psi)

Extraction Apparatus

The apparatus used in separating the organic material from the hardened cement paste or concrete was a Soxhlet extraction assembly. The assembly consisted of a 500 ml flat-bottom flask, grinding No. 24/40, connected to a soxhlet extractor, inside diameter of 50 mm; this in turn was connected to a large Friederichs condenser, grinding No. 55/50. The entire assembly was mounted on a Vari-Heat hot plate. The size of the extraction thimble contained in the Soxhlet extractor was 123 x 43 mm.

High Pressure Liquid Chromatograph

The separation, characterization, and identification of the organic material extracted from hardened cement paste or concrete was accomplished using a Waters ALC/GPC 201 high pressure liquid chromatograph, shown in Figure 1. A flow diagram of the major components of this system is shown in Figure 2.

The pump used in this system is a Milton Roy constant flow high pressure pump. illustrated in Figure 3. It operates at pressures to 3000 psi and at flow rates of 0.30 to 2.70 ml./min. This constant displacement pump also maintains the necessary restrictors and accumulators for flow damping.

The injector used was a Waters Model U6K, universal liquid chromatograph injector, shown in Figure 4. The U6K injector is a septumless injector that enables the user to load samples and make injections at atmospheric pressure, while solvent is simultaneously being delivered to the system at full pressure (up to 6000 psi) without interruption of solvent flow.

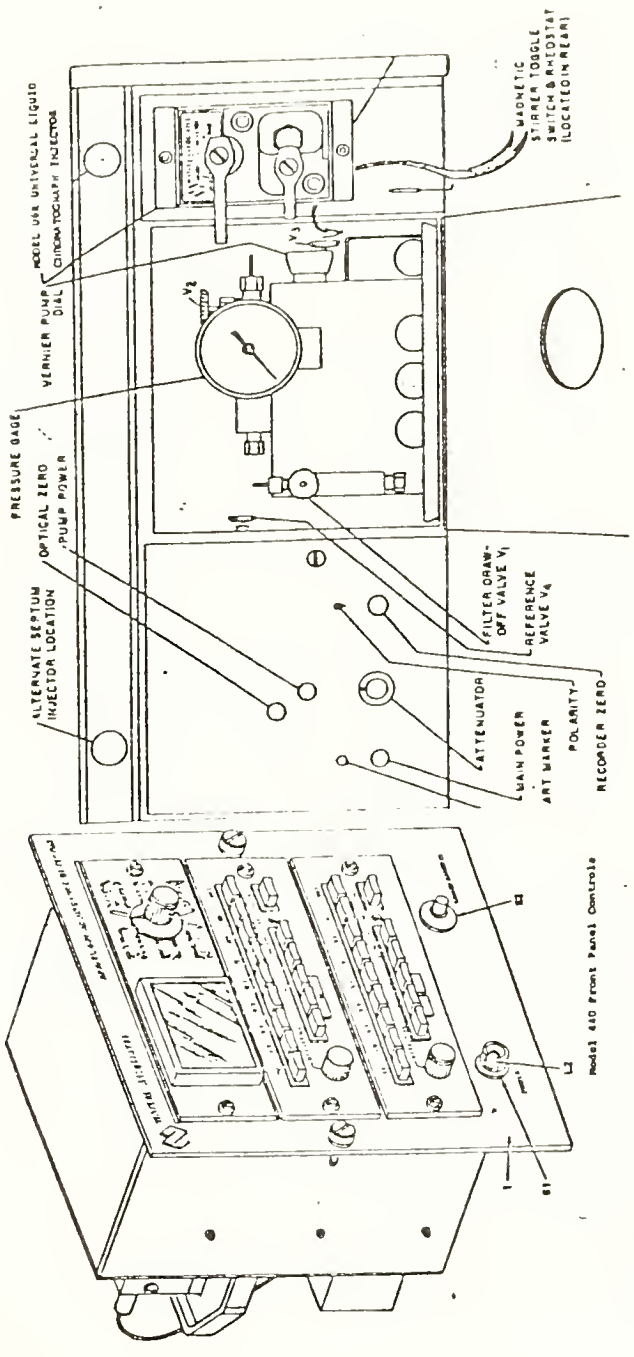


Figure 1 - HPLC System Including Free Standing UV Absorbance Detector.

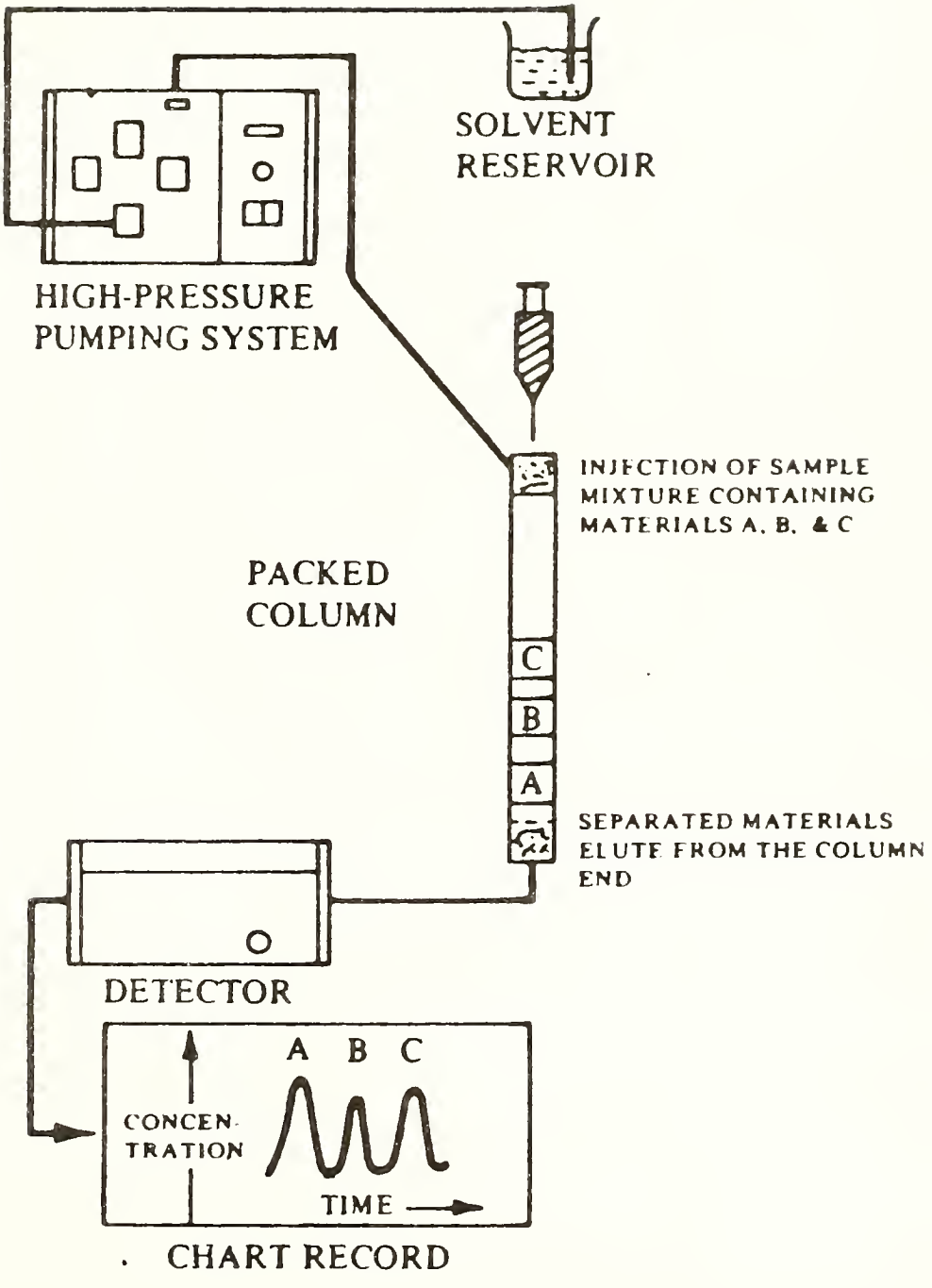


Figure 2 - HPLC Flow Diagram

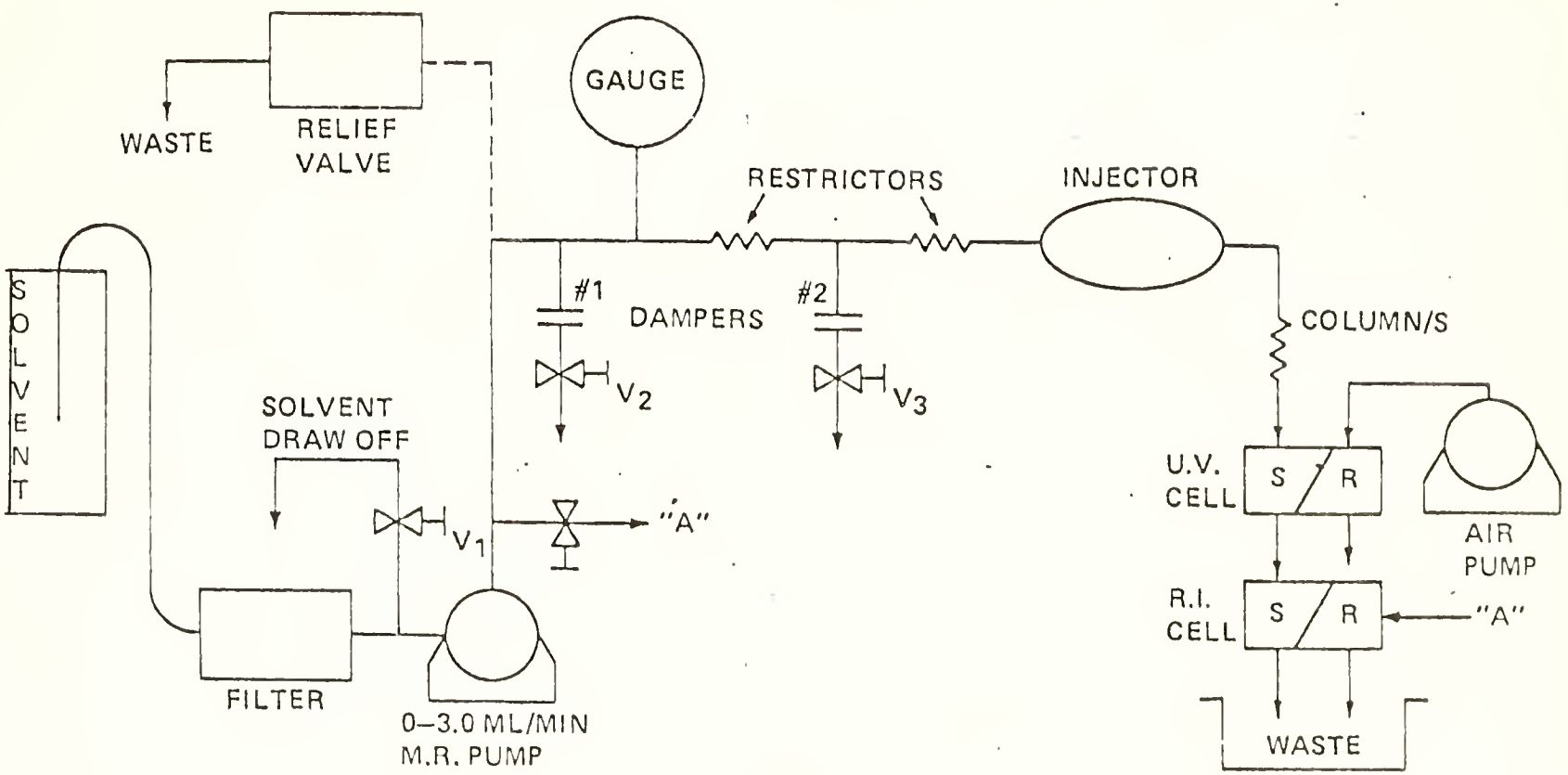


Figure 3 - HPLC Constant Displacement Pump

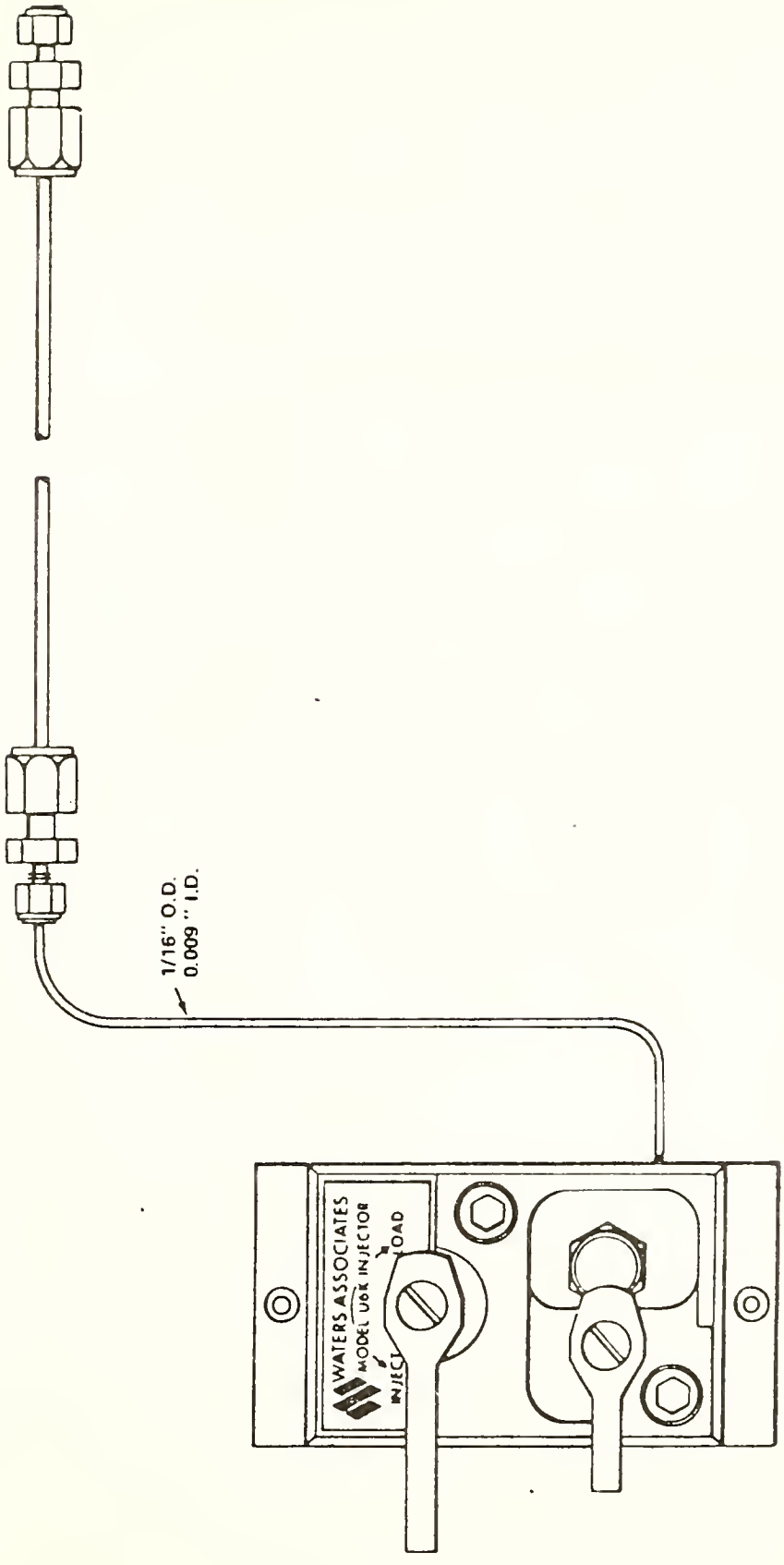


Figure 4 - Waters Model U6K Injector and LiChrosorb RP-18 Column

The pre-packed columns were purchased from EM Laboratories, Inc., an associate of E. Merck, Darmstadt, Germany. The columns were of stainless steel, 250 mm in length and with an inside diameter of 4.6 mm. The column packings designated as Hibar II, RP-18, were used in the reverse phase mode. LiChrosorb RP-18 is a non-polar organic coating that is chemically bonded to a silica gel support by reacting the silica gel with dioctadecyldichlorosilane.

A guard column, 13 cm in length and 2 mm i.d. was dry-packed with LiChrosorb RP-2, 30-40 um. LiChrosorb RP-2 is a dimethylsilane phase chemically bonded to a silica gel base. The guard column was used to protect the analytical column from extraneous materials in the sample that could change the performance characteristics of the analytical column.

The HiBar II, LiChrosorb RP-18, 10 um analytical column was pretested for theoretical plate count. The data are given in Figure 5. The number of theoretical plates is a measure of band spread of a peak throughout the chromatographic system. The higher the number of theoretical plates, the smaller the band spread, and thus the more efficient the column for separation. The number of theoretical plates obtained was 19,120 plates/meter and 4,780 plates for a 25 cm column.

A dual detector system consisting of a differential refractometer (RI), and an ultraviolet absorbance detector (UV) was used.

The refractive index detector was Waters Model R-401, schematically illustrated in Figure 6. It records the deflection of a light beam due to the differences in refractive index between the sample and the reference liquids in a single compact sample cell. The R-401 differential

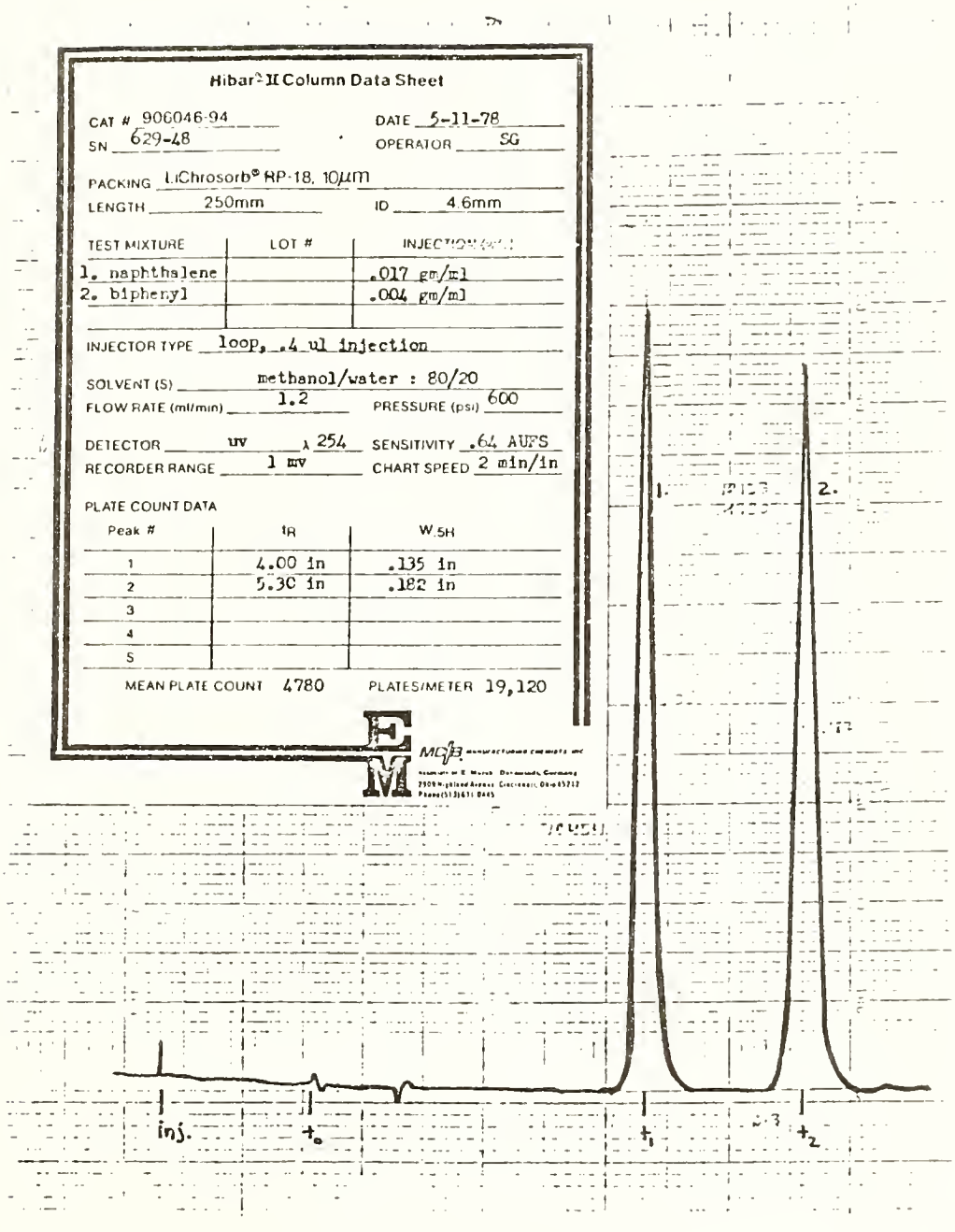


Figure 5 - LiChrosorb RP-18 Hibar II Column Data

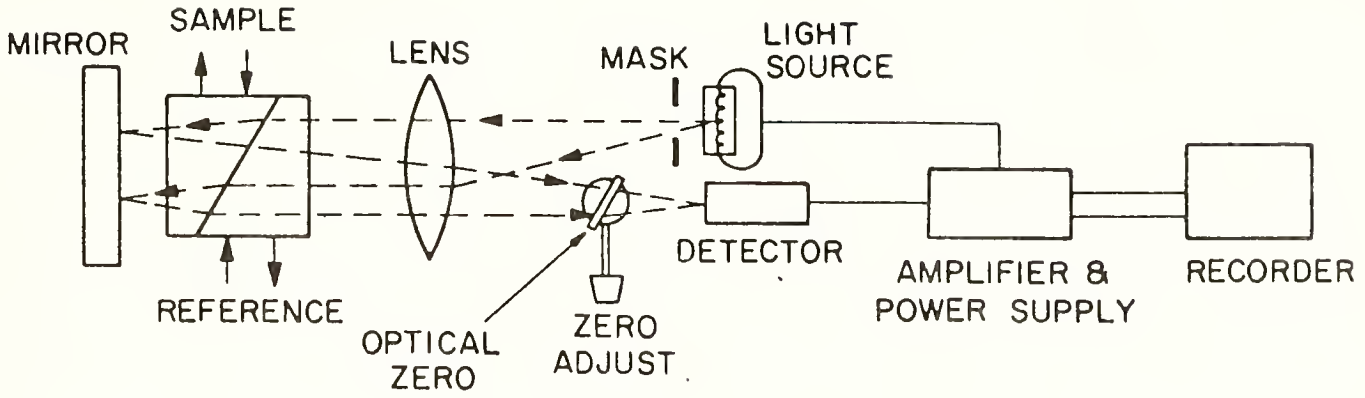


Figure 6 - Waters R-401 Differential Refractive Index Detector

refractometer is constructed within a massive heat exchanger block that minimizes the effects of flow, pressure, and temperature changes. The sensitivity of the detector is approximately 10^{-7} RI units, which corresponds to a concentration difference of about 1 ppm.

The Ultraviolet Absorbance detector was Waters Model 440, schematically shown in Figure 7. It is a standard, single-channel, 254 nm. wavelength detector assembly. The detector sensitivity ranges from 0.005 to 2.0 AUFS with direct digital readout of absorbance.

The output from each detector was monitored by a Houston instrument Ominiscribe strip chart recorder, Model No. 5211-15. This recorder offers either a dual pen mode for a dual detector system or a single pen plus electronic integrator mode for a single detection system.

M440 OPTICS & ELECTRONICS DIAGRAM

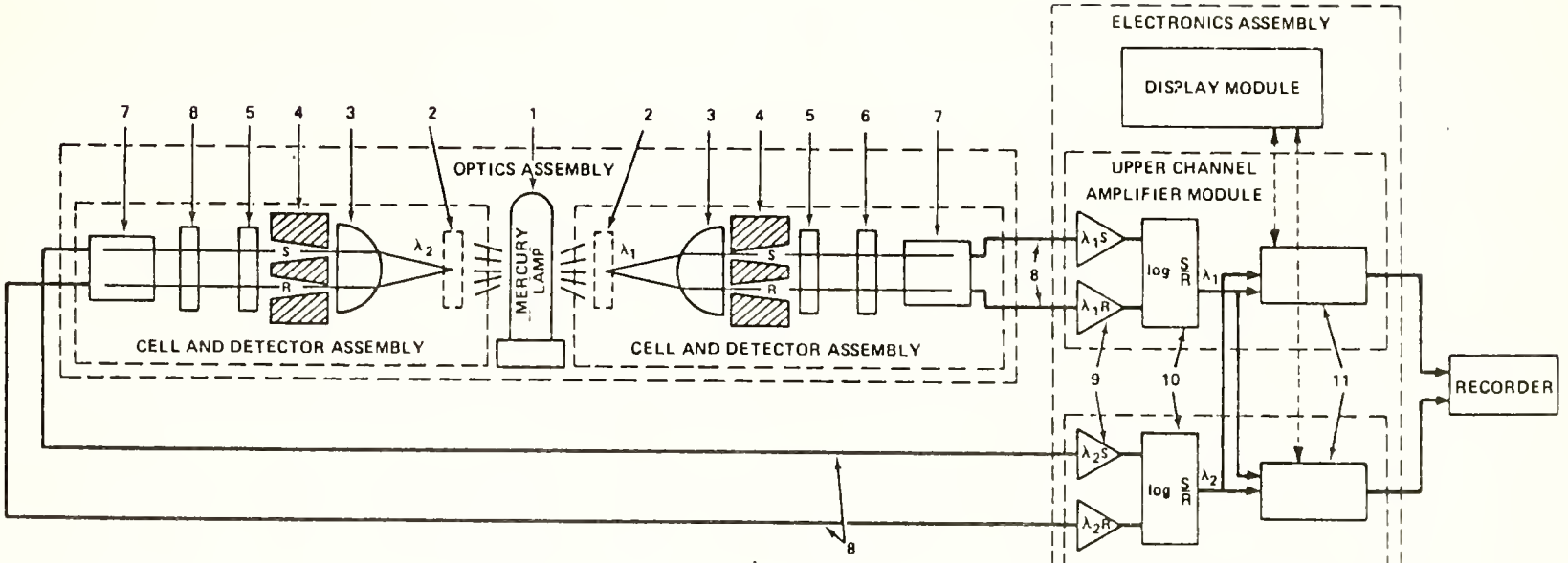


Figure 7 - Waters Model 440 Ultraviolet Absorbance Detector

CHAPTER IV - EXPERIMENTAL

This section describes the analytical technique, as finally evolved. Various considerations during this evolution are described in the Discussion section.

Sample Preparation

Cement paste samples were prepared using admixtures at dosage rates comparable to those used in the field. Mix proportions and dosage rates are given in Table 3. The appropriate amount of admixture was dissolved in deionized water and made up to a total volume of 400 ml. When more than one admixture was used, the appropriate amount of each was dissolved in 200 ml of deionized water. Both these solutions were then combined in the mixing bowl prior to the addition of the cement. Sometimes other admixtures cannot be mixed together with air-entraining agents, owing to precipitation that results in a loss of the effect they otherwise would have. The mix proportions and dosage rates for the samples are given in Table 4.

Subsequent to the addition of the admixture solutions to the mixing bowl, 1000 g of portland cement ASTM Type I, lab number 323, was introduced and mixed according to ASTM C-305.

The cement paste was molded in a 3 x 6-in. paper mold, as described in ASTM C-470. The hardened samples were demolded after 24 h and placed in a fog room at a temperature of 23^{o}C for 28 days.

Table 3 - Cement Paste Mix Designs for Single Admixtures

Code Letter	Dosage Rate Used fl. oz/100#	Weight of Admixture, g.	Weight of Cement, g.	Volume of Water, ml.	W/C
A	1.5	1.0	1000	400	0.4
B	4.0	2.5	1000	400	0.4
C	3.0	2.0	1000	400	0.4
D	1.5	1.0	1000	400	0.4
E	7.0	4.4	1000	400	0.4
F	3.0	2.0	1000	400	0.4
G	9.0	5.7	1000	400	0.4
H	3.0	2.0	1000	400	0.4
I	3.0	2.0	1000	400	0.4
J	2.0#	20.0	1000	400	0.4
K	1.5	1.0	1000	400	0.4
L	4.0	2.5	1000	400	0.4
M	4.0	2.5	1000	400	0.4
N	24.0	15.0	1000	400	0.4
O	3.0	2.0	1000	400	0.4
P	19.0	12.0	1000	400	0.4
Q	20.0	12.5	1000	400	0.4
R	32 fl. oz of 2% soln.	20g of 2% soln.	1000	400	0.4
S	1.5% by weight	15g	1000	400	0.4
T	0.05% by weight	0.5g	1000	400	0.4
Control	--	--	1000	400	0.4

Table 4 - Cement Paste Mix Designs for Combinations of Admixtures

Code Letter	Admixtures Types	Dosage Rates Used fl. g/100#	Weight of Admixtures, g	Weight of Cement, g	Volume of Water, ml	W/C
A-B	AEA* - Type A	1.5 - 4.0	1.0 - 2.5	1000	400	0.4
A-C	AEA - Type D	1.5 - 3.0	1.0 - 2.0	1000	400	0.4
D-E	AEA - Type A	1.5 - 7.0	1.0 - 4.4	1000	400	0.4
D-F	AEA - Type A	1.5 - 3.0	1.0 - 2.0	1000	400	0.4
D-G	AEA - Type D	1.5 - 9.0	1.0 - 5.7	1000	400	0.4
D-H	AEA - Type D	1.5 - 3.0	1.0 - 2.0	1000	400	0.4
D-I	AEA - Type D	1.5 - 3.0	1.0 - 2.0	1000	400	0.4
D-J	AEA - Type C	1.5 - 2.0% by wt	1.0 -20.0	1000	400	0.4
K-L	AEA - Type A	1.5 - 4.0	1.0 - 2.5	1000	400	0.4
K-M	AEA - Type B	1.5 - 4.0	1.0 - 2.5	1000	400	0.4
K-N	AEA - Type C	1.5 -24.0	1.0 -15.0	1000	400	0.4
K-O	AEA - Type D	1.5 - 3.0	1.0 - 2.0	1000	400	0.4
K-P	AEA - SWR**	1.5 -19.0	1.0 -12.0	1000	400	0.4
D-Q	AEA - SWR	1.5 -20.0	1.0 -12.5	1000	400	0.4
A-R	AEA - SWR	1.5 -24.0	1.0 -15.0	1000	400	0.4

* AEA - An air-entraining agent

** SWR - A super water-reducer

Extraction

A 1-1½ in. slice was sawed from the hardened cement paste cylinder and then crushed in a jaw crusher. The analytical sample to be extracted was obtained by sieving the crushed sample. The sample used passed the number 4 (4.75 mm) sieve and was retained on the number 16 (1.19 mm). This fraction of the crushed sample was then oven dried at 110°C for 24 h.

Fifty grams of the oven-dried standard cement paste sample was weighed to the nearest 0.1 g and placed in a large Soxhlet extraction thimble (123 mm x 43 mm). The thimble was then placed in the Soxhlet apparatus. The extraction solvent was 75 percent methylethyl ketone, 14 percent absolute ethanol, and 11 percent water. This mixture is a ternary azeotrope with a boiling point of 73.2°C. Two hundred ml were placed in a 500 ml flat-bottom flask with a standard taper neck. This was attached to the Soxhlet (no grease) and the extraction of the admixture from the sample was carried out for 12 h. Heating was with a suitable hot plate. The flask, soxhlet extractor, and condensor were covered entirely with aluminum foil in order to provide even heat distribution.

Chromatographic Sample Preparation

After cooling, the extraction solution was poured off into a 500 ml evaporating dish. The solvent was evaporated to dryness on a hot plate at a temperature below its boiling point. The residue was allowed to cool, then 10 ml of the mobile phase were added. This liquid was 80 percent acetonitrile and 20 percent water, by volume. The solution was swirled in the dish for 2 min. and then poured into a test tube.

The procedure was repeated with 5 milliliters of mobile phase and swirling for 1 minute. The extracts were combined and filtered through a Waters "Sample Clarification Kit", illustrated in Figure 8. The filtration uses a syringe delivering device and a 13 mm Nucleopore polycarbonate membrane that removes particulate matter larger than 0.4 um.

Chromatographic Procedure

During the following description of the procedure the reader should refer to the sketch of the apparatus shown in Figure 1 and 3.

The "HPLC", the UV detector, and the recorder were allowed the appropriate warm up period recommended by the manufacturers. Meanwhile, approximately fifty milliliters of mobile phase was purged through valve V_1, which changes the liquid in the inlet filter and removes air from the filter. With the vernier dial at 100 (maximum flow rate), the pump was started and vent valve V_2 was opened for 3-5 minutes. Then V_2 was closed and V_3 was opened for 3-5 min. and then closed. Vent valves V_2 and V_3 were used to vent the dampers and pressure gauge to assure that the liquid in the damper was the same as the liquid being pumped by the pump. This is necessary to get a constant, low noise baseline when using the refractometer detector.

Next the reference valve was opened for 10-15 minutes. The reference valve permits flushing of the reference side of the refractometer with solvent. Then this valve was closed, the vernier dial was set to 30, which corresponds to a flow rate of 1.1 milliliters per minute for a mobile phase with a composition such as the one used. The mobile phase was allowed to flow through the column equilibrating the stationary phase with solvent for 15-30 minutes.

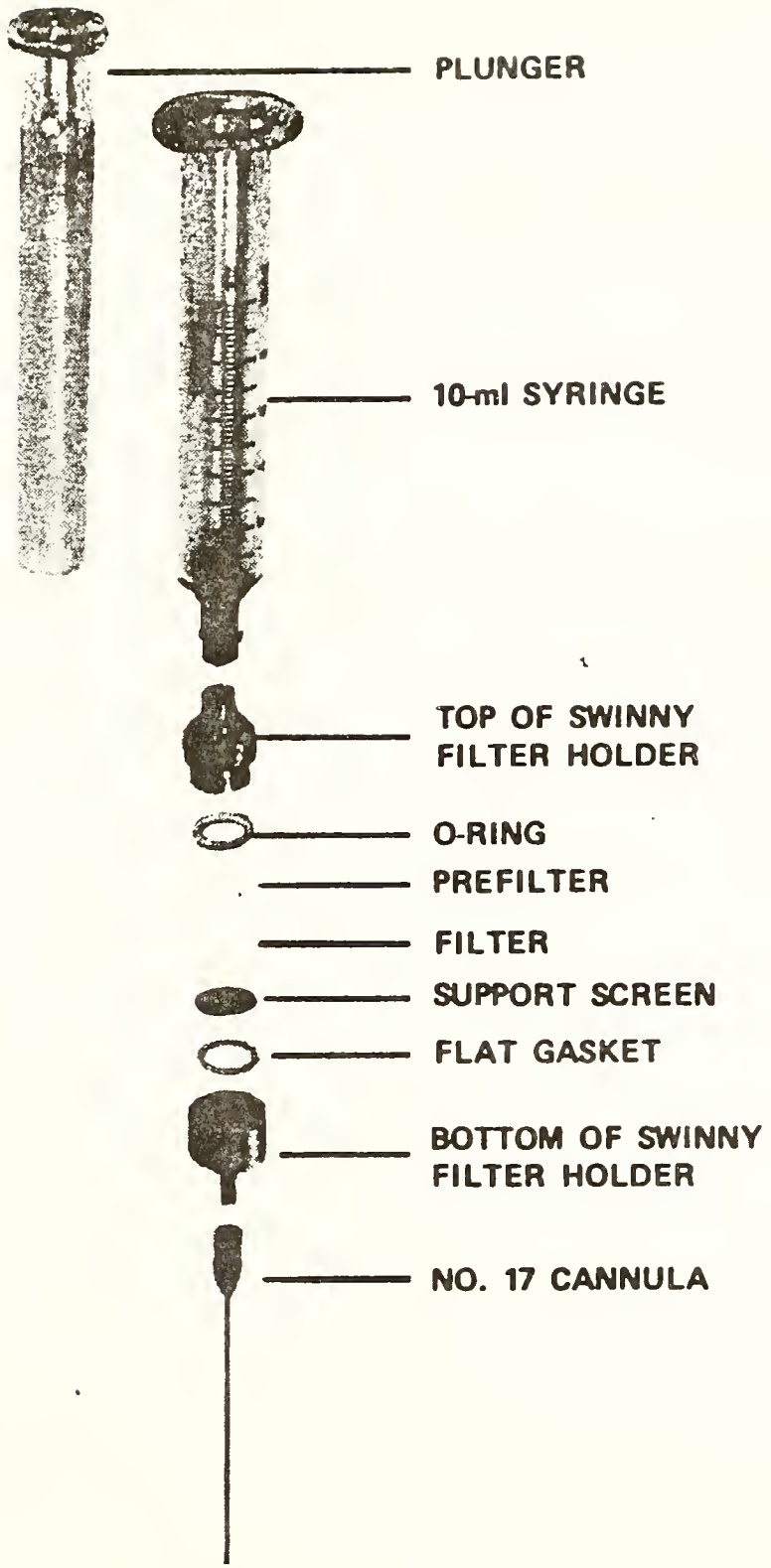


Figure 8 - Waters Sample Clarification Kit Assembly

The described procedure is necessary for starting up the equipment at the beginning of the day and need not be repeated prior to every sample injection. The procedure is also necessary when recharging the equipment with either freshly prepared mobile phase or when changing solvents or solvent compositions.

The final step was injecting the filtered sample into the stream of flow and onto the column. A Hamilton 701-N, 10 microliter syringe with a needle point that is 2 inches in length and has diameter of 0.020 inches was used. This is important when using the Waters U6K injector, because the injection port is made to accommodate only that size of needle.

The Waters model U6K has two exposed levers, one on the top and one on the bottom, as shown in Figure 4. When the top lever is at 3 o'clock with respect to the vertical (load position), and the bottom lever is at 9 o'clock, valves A, B, and C are closed and the injector mode is in the by-pass configuration, Figure 9. To load the sample, the bottom lever was moved counter-clockwise to 6 o'clock, thus opening valve C, and the sample loading plug was removed. The syringe was inserted and the appropriate amount of sample was injected, displacing the same volume of liquid out the vent tube, Figure 10. Next, the syringe was removed, the sample loading plug was reinserted, and the bottom lever was returned to the 9 o'clock position, which again closed valve C. The top lever was then moved counterclockwise to the 9 o'clock (Inject) position, which opened valves A and B and allowed the sample to be swept into the stream of flowing mobile phase toward the column inlet, Figure 11.

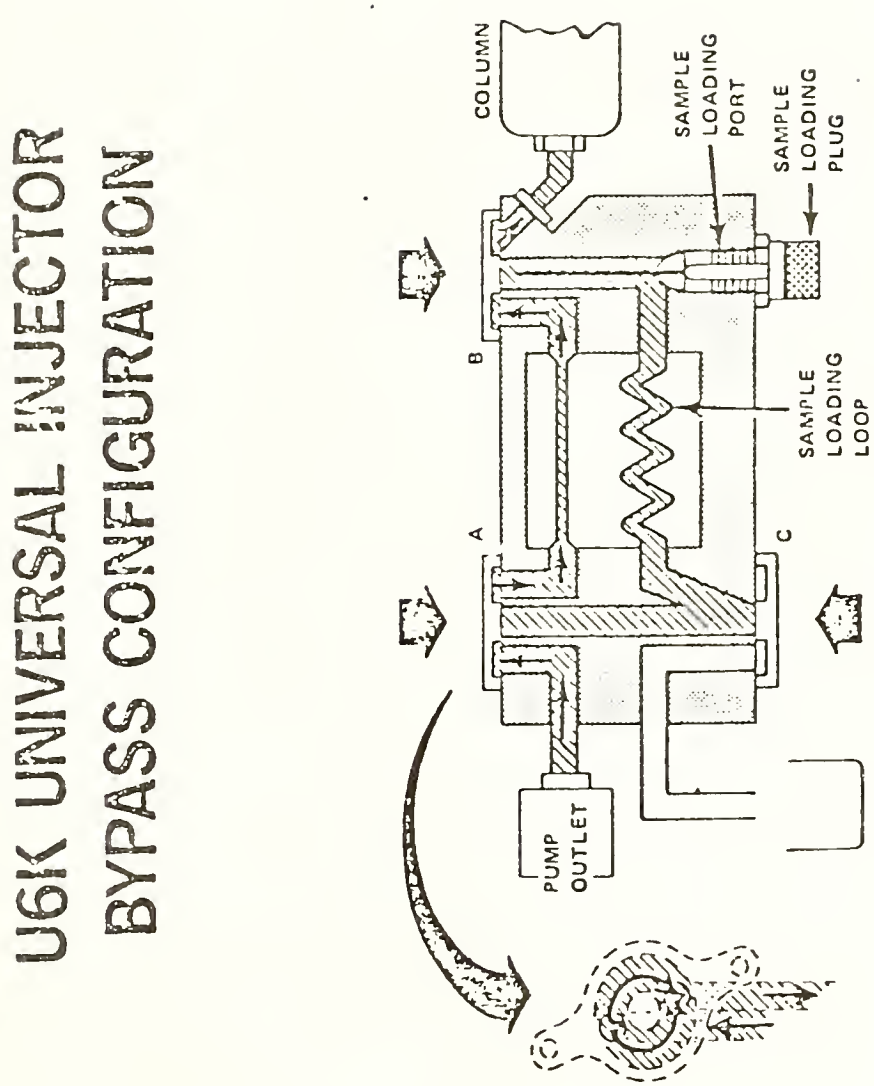


Figure 9 - Waters U6K Injector - By-pass Mode

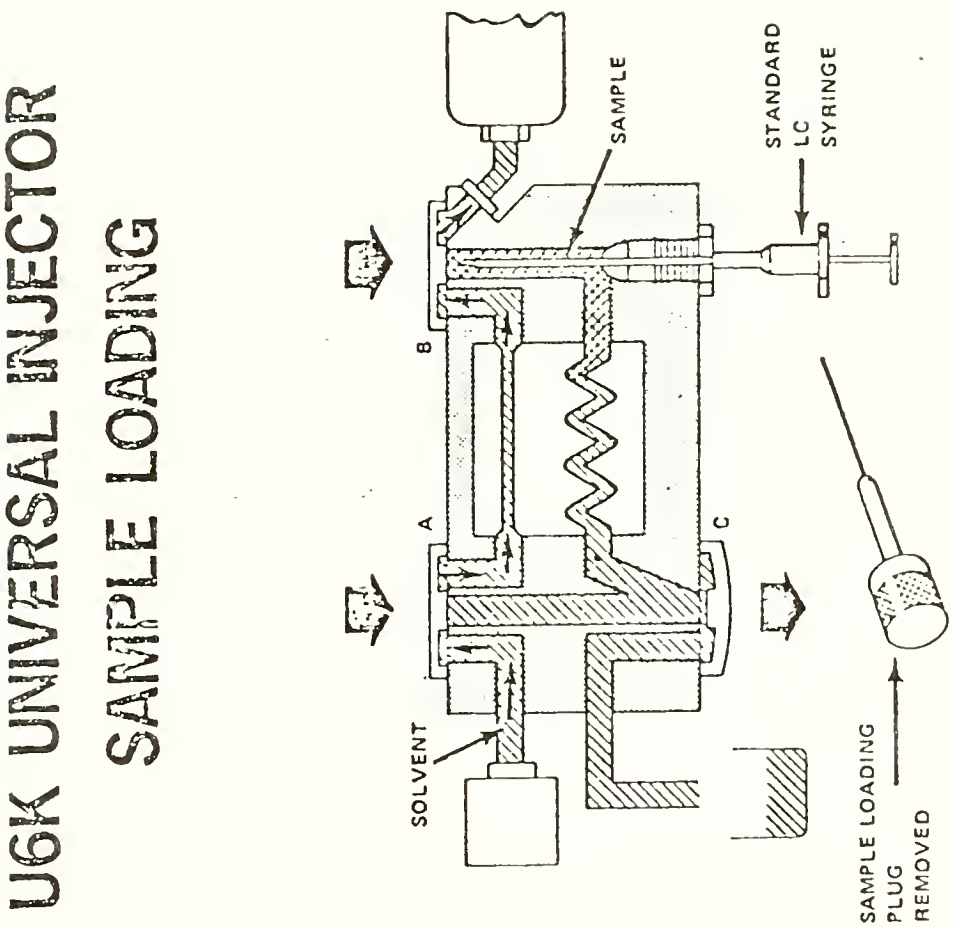


Figure 10 - Waters U6K Injector - Sample Loading

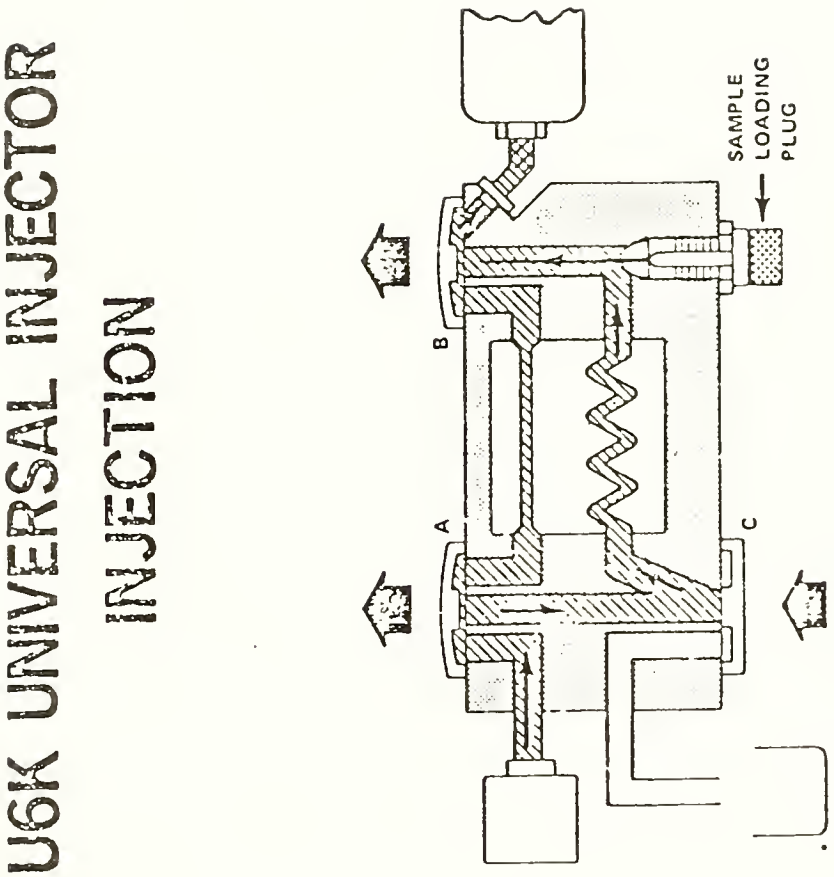


Figure 11 - Waters U6K Injector - Injection

Using approximately the same length of column, flow rate, and dual detector system, a complete chromatogram is recorded in less than eight minutes from the time of injection. The time of injection is marked on the recorder chart when the top level of the U6K injector is turned to the Inject position.

CHAPTER V - EXPERIMENTAL RESULTS

The following figures represent the results of the chromatographic data obtained from the organic material extracted from the hardened standard cement pastes. The figures are shown in two parts. The first part is the chromatograms obtained from the organic material extracted from hardened pastes containing only a single admixture. Part two shows chromatograms obtained from the organic material extracted from hardened pastes containing an air-entraining agent and another admixture type.

Part 1.

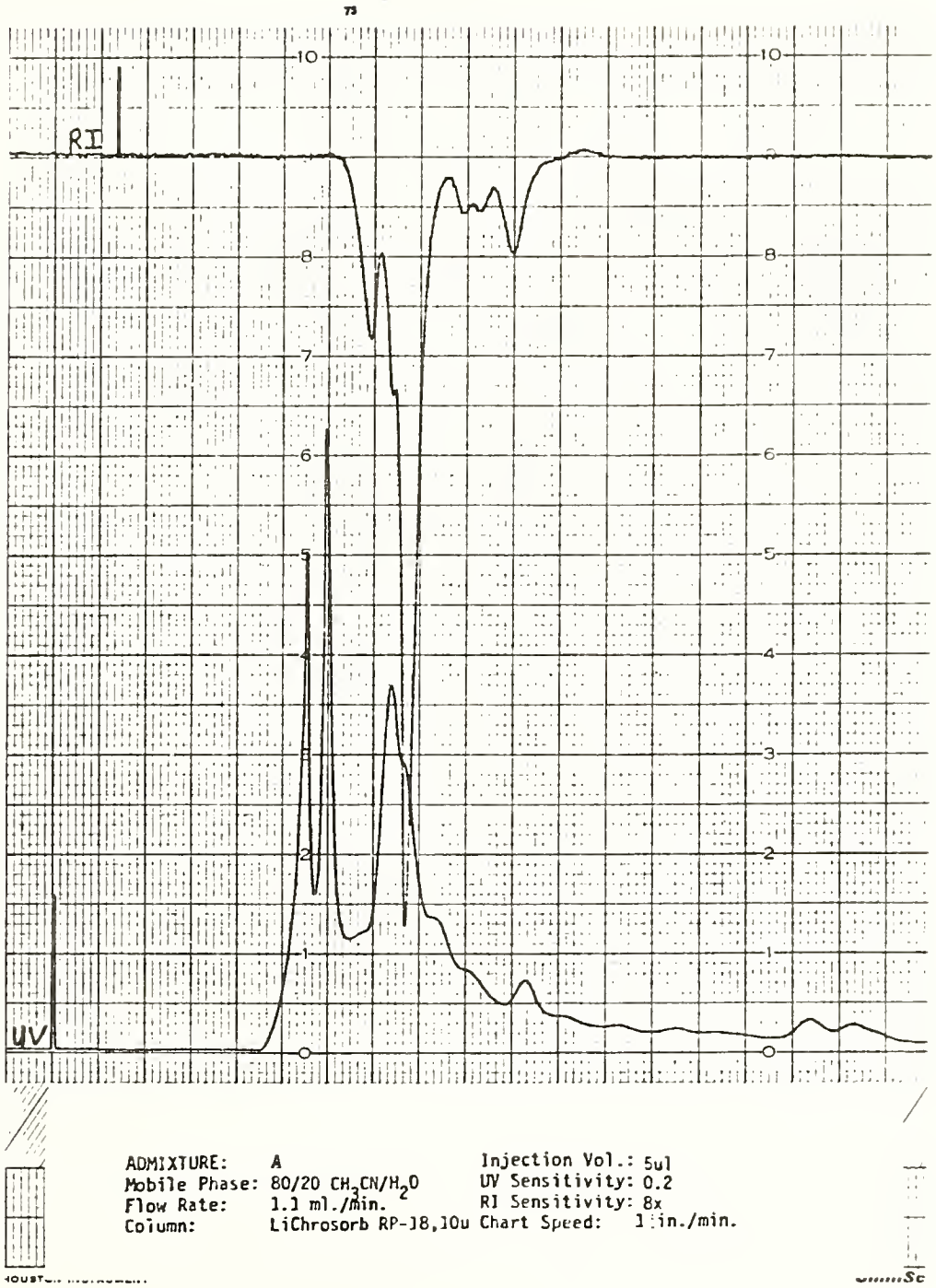
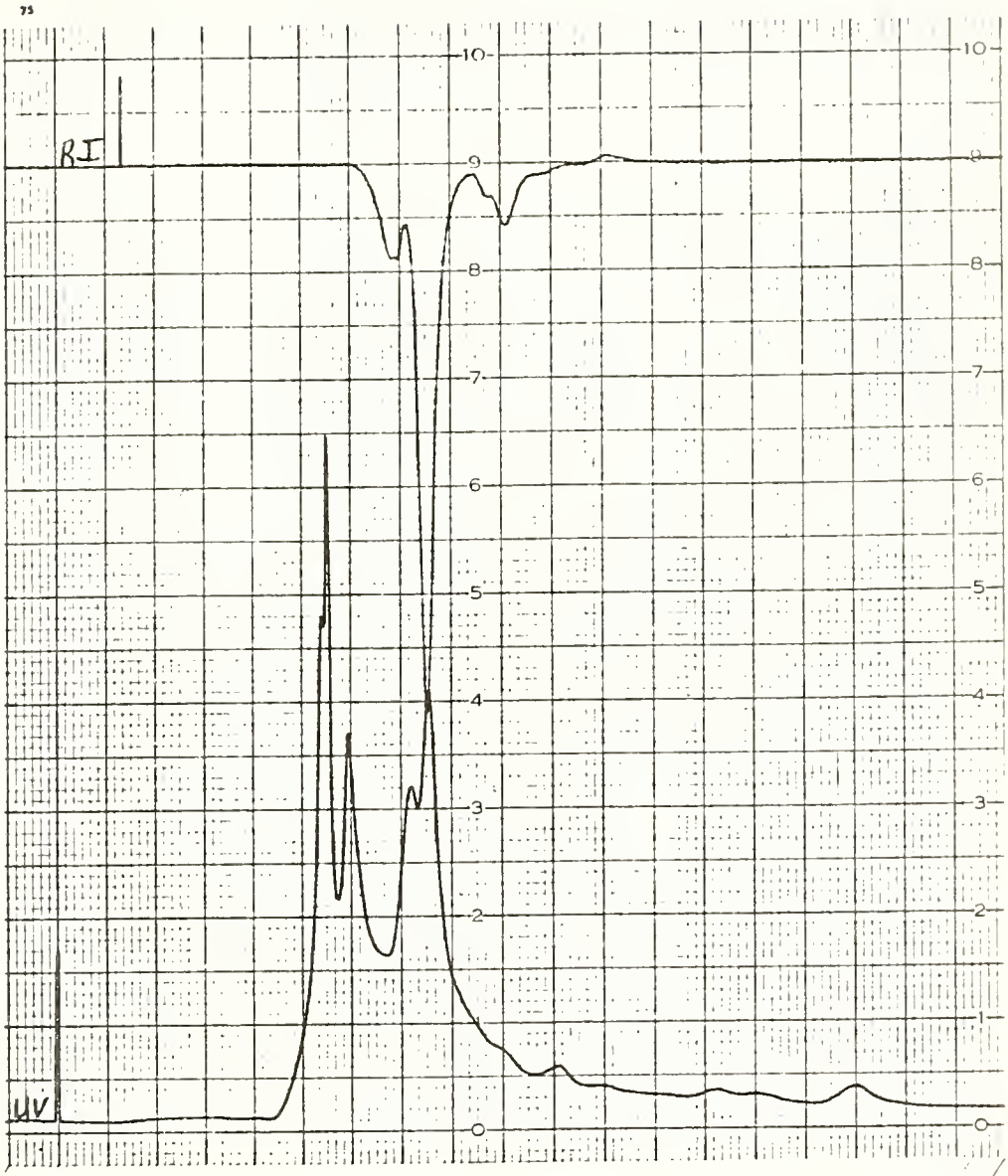


Figure - 13



ADMIXTURE: D
Mobile Phase: 80/20 CH_3CN/H_2O
Flow Rate: 1.1 ml./min.
Column: LiChrosorb RP-18,10u
Injection Vol.: 10ul
UV Sensitivity: 0.2
RI Sensitivity: 16x
Chart Speed: 1 in./min.

UniniScribe* CHART TYPE EC 146

Figure - 14

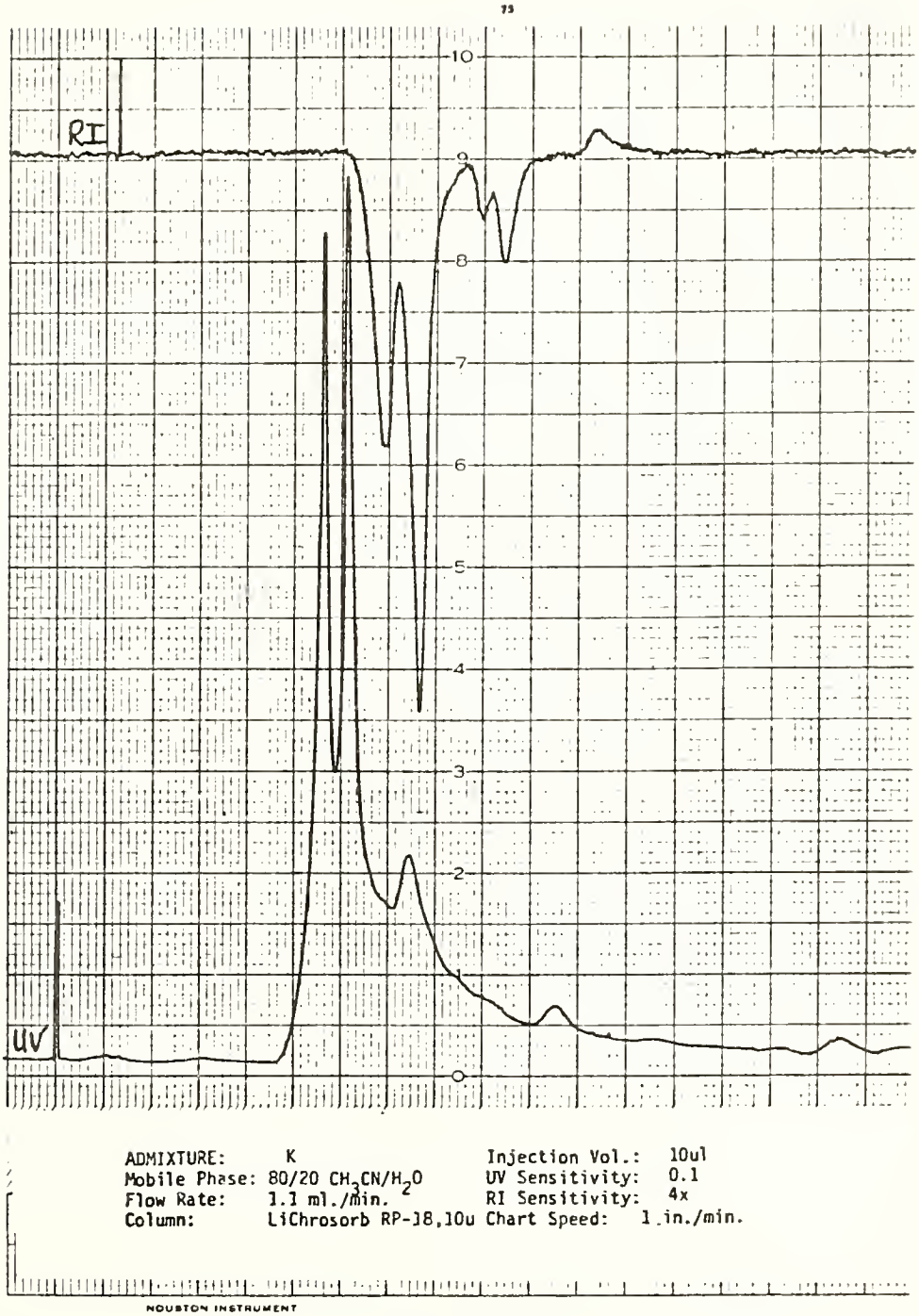
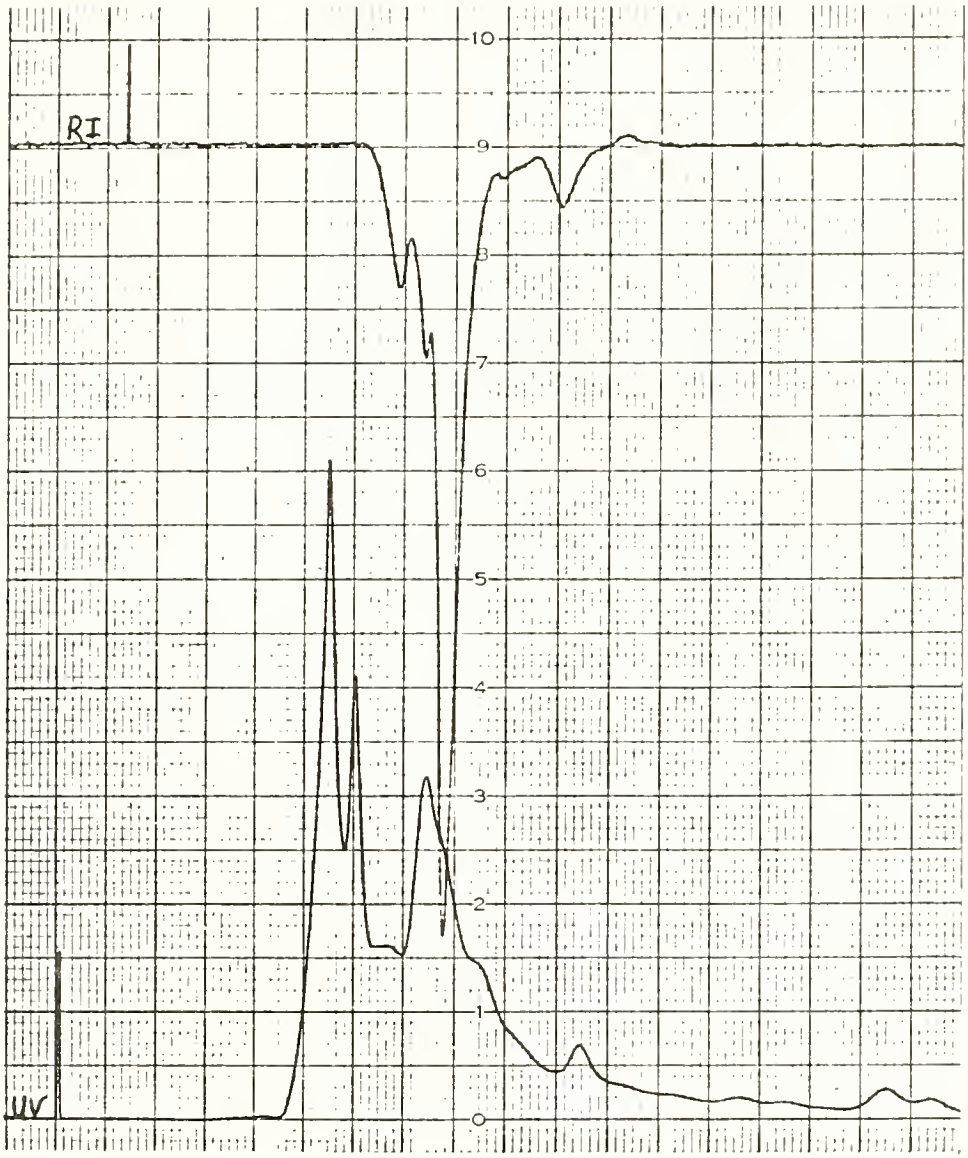

RI
UV
10
9
8
7
6
5
4
3
2
0
ADMIXTURE: K
Mobile Phase: 80/20 CH_3CN/H_2O
Flow Rate: 1.1 ml./min.
Column: LiChrosorb RP-18,10u
Injection Vol.: 10ul
UV Sensitivity: 0.1
RI Sensitivity: 4x
Chart Speed: 1 in./min.
HOUSTON INSTRUMENT

Figure - 15



ADMIXTURE: B
Mobile Phase: 80/20 CH_3CN/H_2O
Flow Rate: 1.1 ml./min.
Column: LiChrosorb RP-18,10u
Injection Vol.: 5ul
UV Sensitivity: 0.1
RI Sensitivity: 8x
Chart Speed: 1 in./min.

OmniScribe® CHART TYPE EC 14R HOUSTON INSTRUMENT

Figure - 16

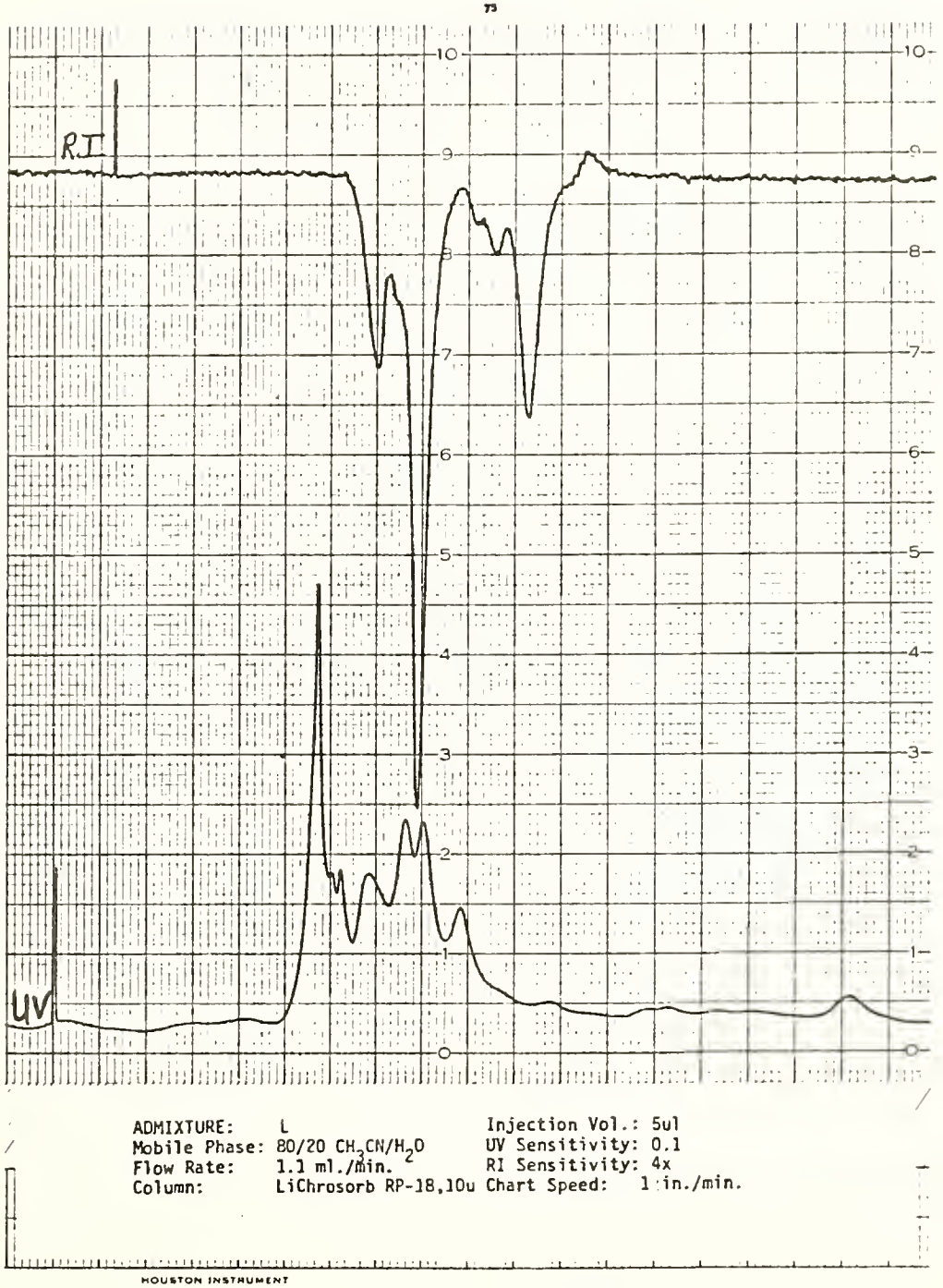

RI
UV
10
9
8
7
6
5
4
3
2
1
0
ADMIXTURE: L
Mobile Phase: 80/20 CH_3CN/H_2O
Flow Rate: 1.1 ml./min.
Column: LiChrosorb RP-18,10u
Injection Vol.: 5ul
UV Sensitivity: 0.1
RI Sensitivity: 4x
Chart Speed: 1 in./min.
HOUSTON INSTRUMENT

Figure - 17

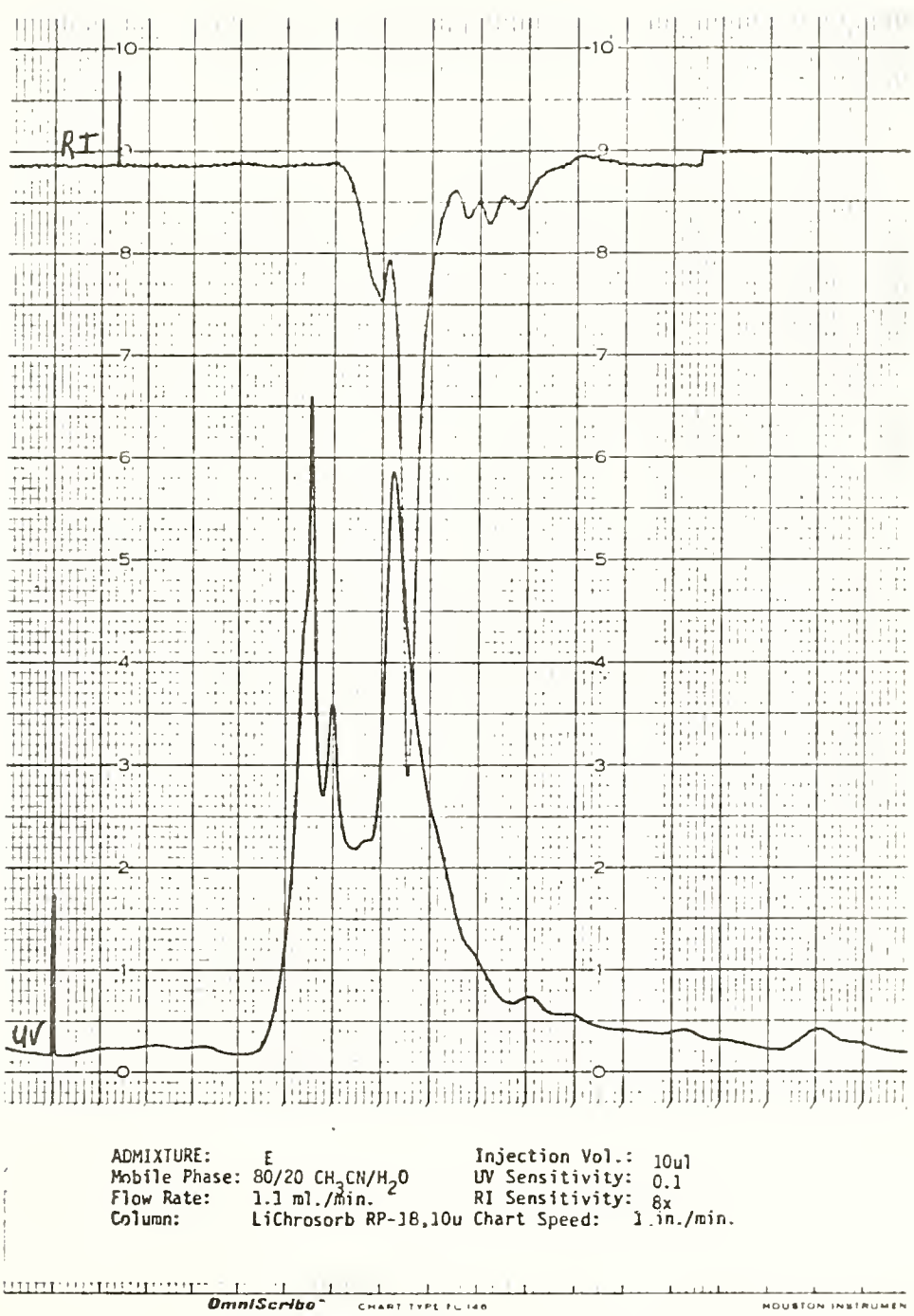
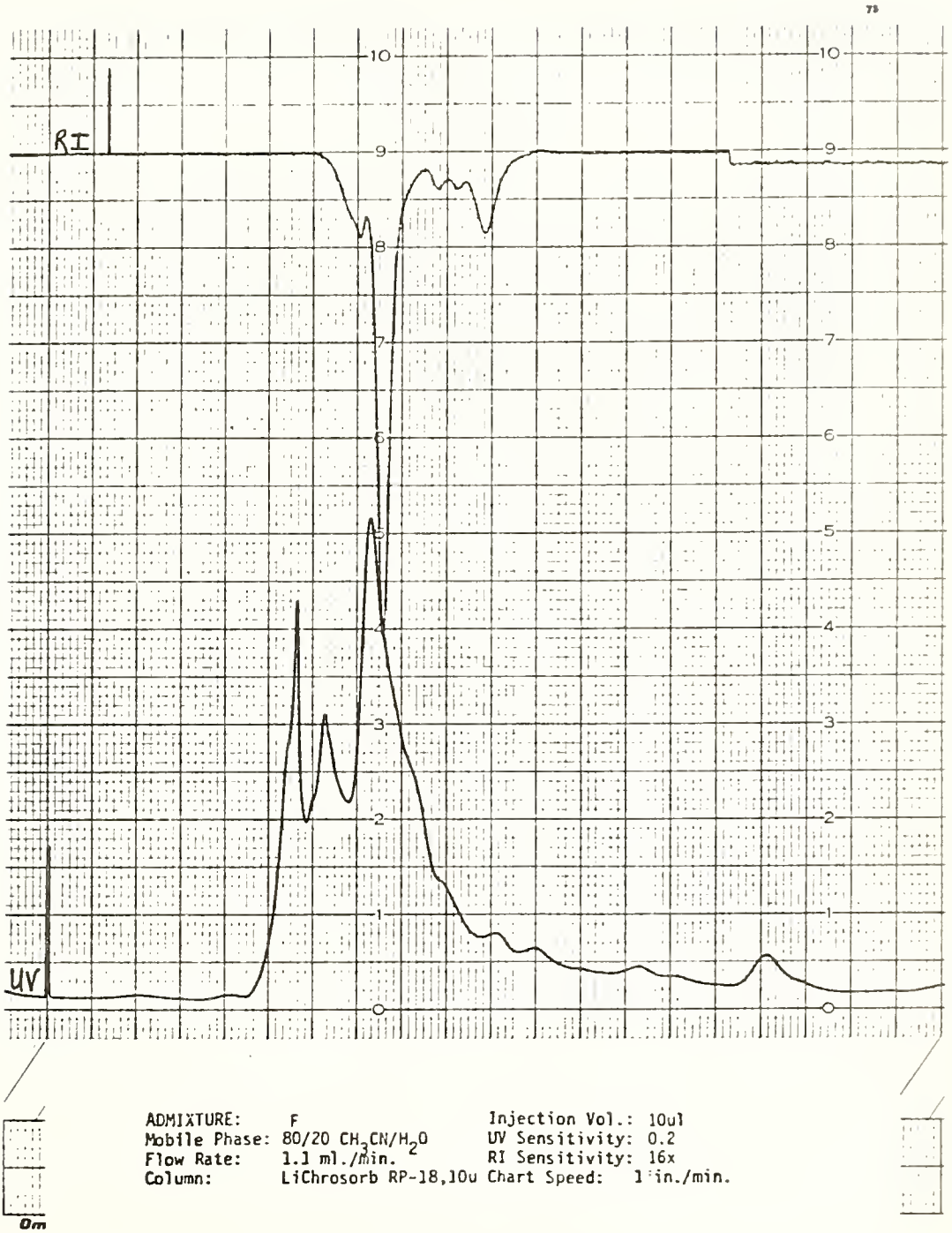
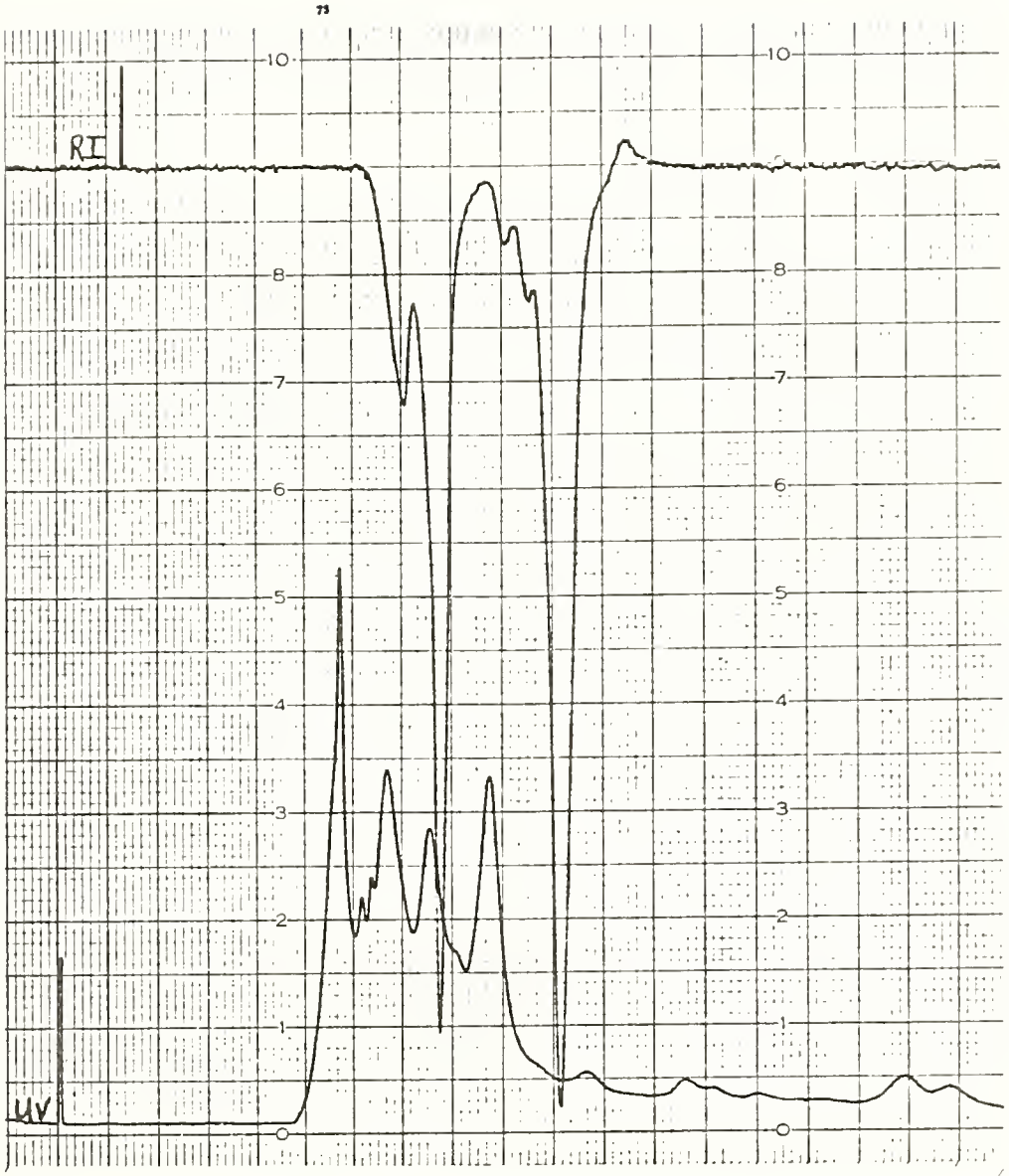

RI
UV
10
8
7
6
5
4
3
2
1
0
ADMIXTURE: E
Mobile Phase: 80/20 CH_3CN/H_2O
Flow Rate: 1.1 ml./min.
Column: LiChrosorb RP-18,10u
Injection Vol.: 10ul
UV Sensitivity: 0.1
RI Sensitivity: 8x
Chart Speed: 1 in./min.
OmniScribe
CHART TYPE PL-146
HOUSTON INSTRUMEN

Figure - 18



ADMIXTURE: F
Mobile Phase: 80/20 CH_3CN/H_2O
Flow Rate: 1.1 ml./min.
Column: LiChrosorb RP-18,10u
Injection Vol.: 10ul
UV Sensitivity: 0.2
RI Sensitivity: 16x
Chart Speed: 1 in./min.

Figure - 19



ADMIXTURE: M
Mobile Phase: 80/20 CH_3CN/H_2O
Flow Rate: 1.1 ml./Min.
Column: LiChrosorb RP-18,10u
Injection Vol.: 10ul
UV Sensitivity: 0.1
RI Sensitivity: 4x
Chart Speed: 1 in./min.

Figure - 20

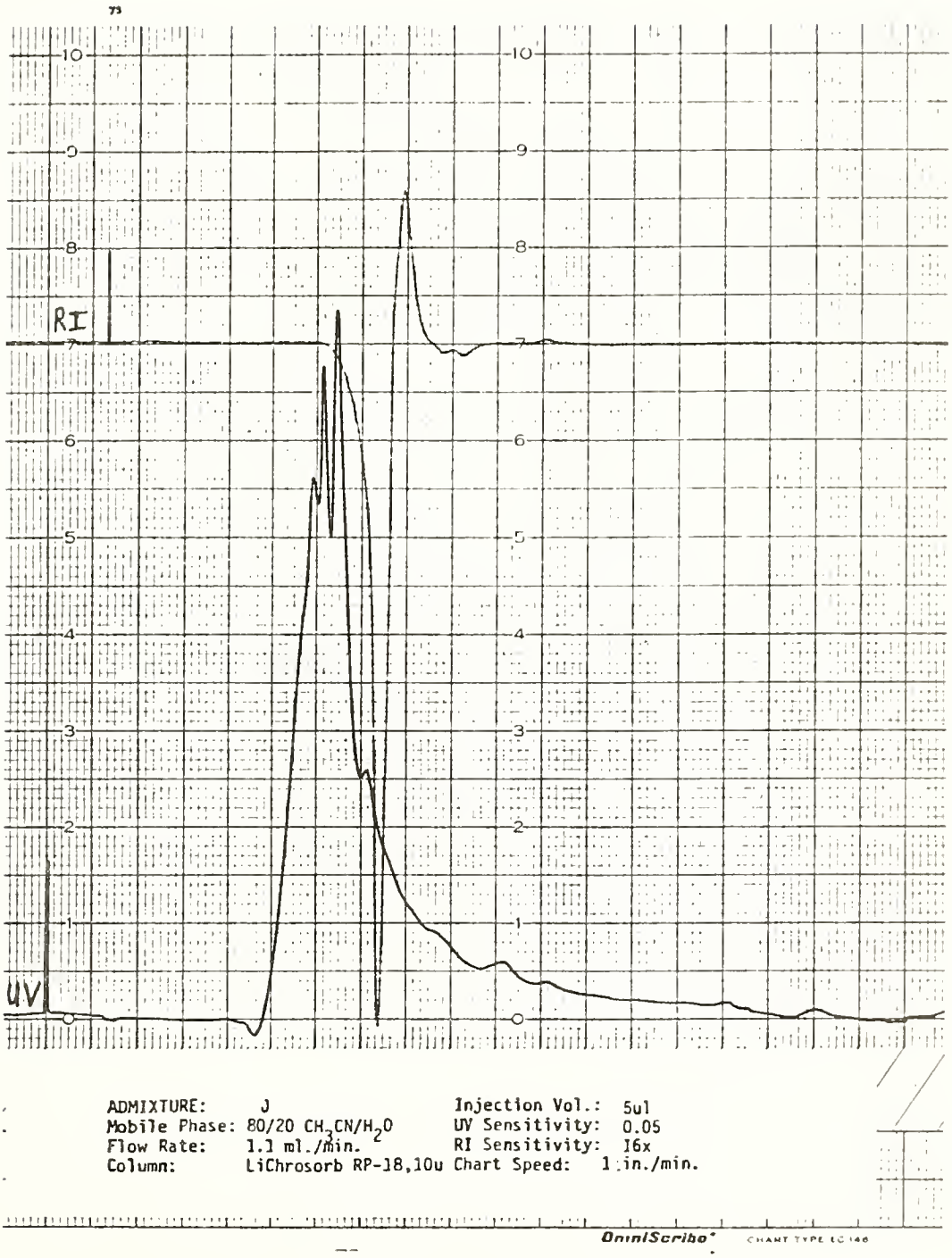
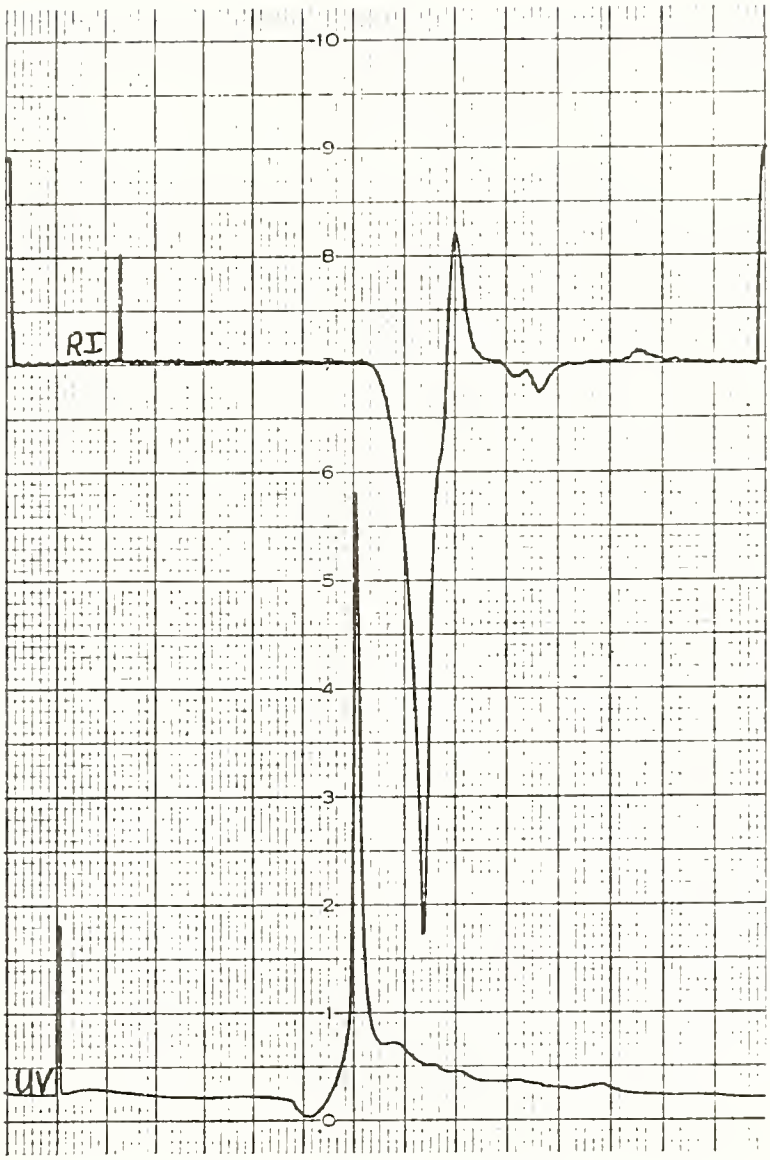

RI
UV
ADMIXTURE: J
Mobile Phase: 80/20 CH_3CN/H_2O
Flow Rate: 1.1 ml./min.
Column: LiChrosorb RP-18,10u
Injection Vol.: 5ul
UV Sensitivity: 0.05
RI Sensitivity: 16x
Chart Speed: 1 in./min.
OmniScribe

Figure - 21

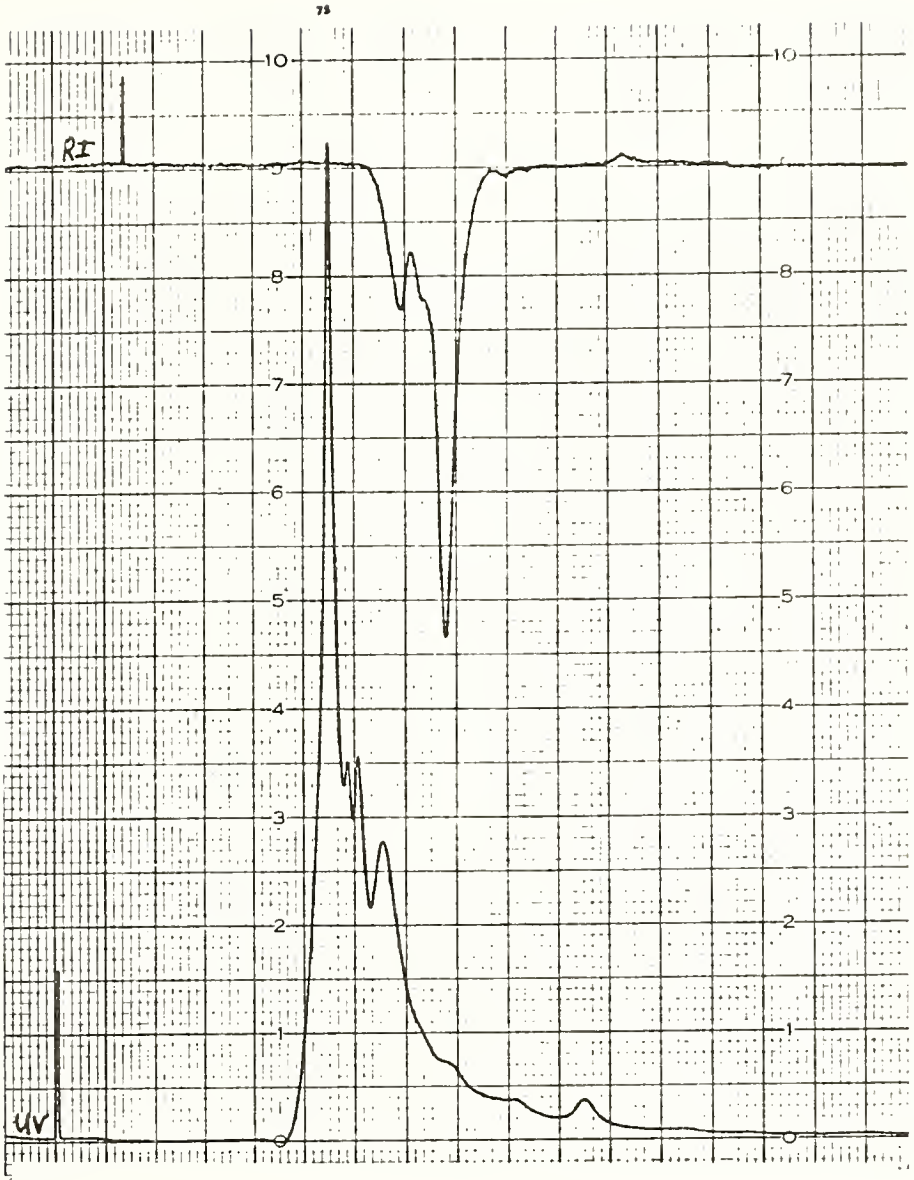


ADMIXTURE: N
Mobile Phase: 80/20 CH_3CN/H_2O
Flow Rate: 1.1 ml./min.
Column: LiChrosorb RP-18,10u

Injection Vol.: 5ul
UV Sensitivity: 0.1
RI Sensitivity: 8x
Chart Speed: 1 in./min.

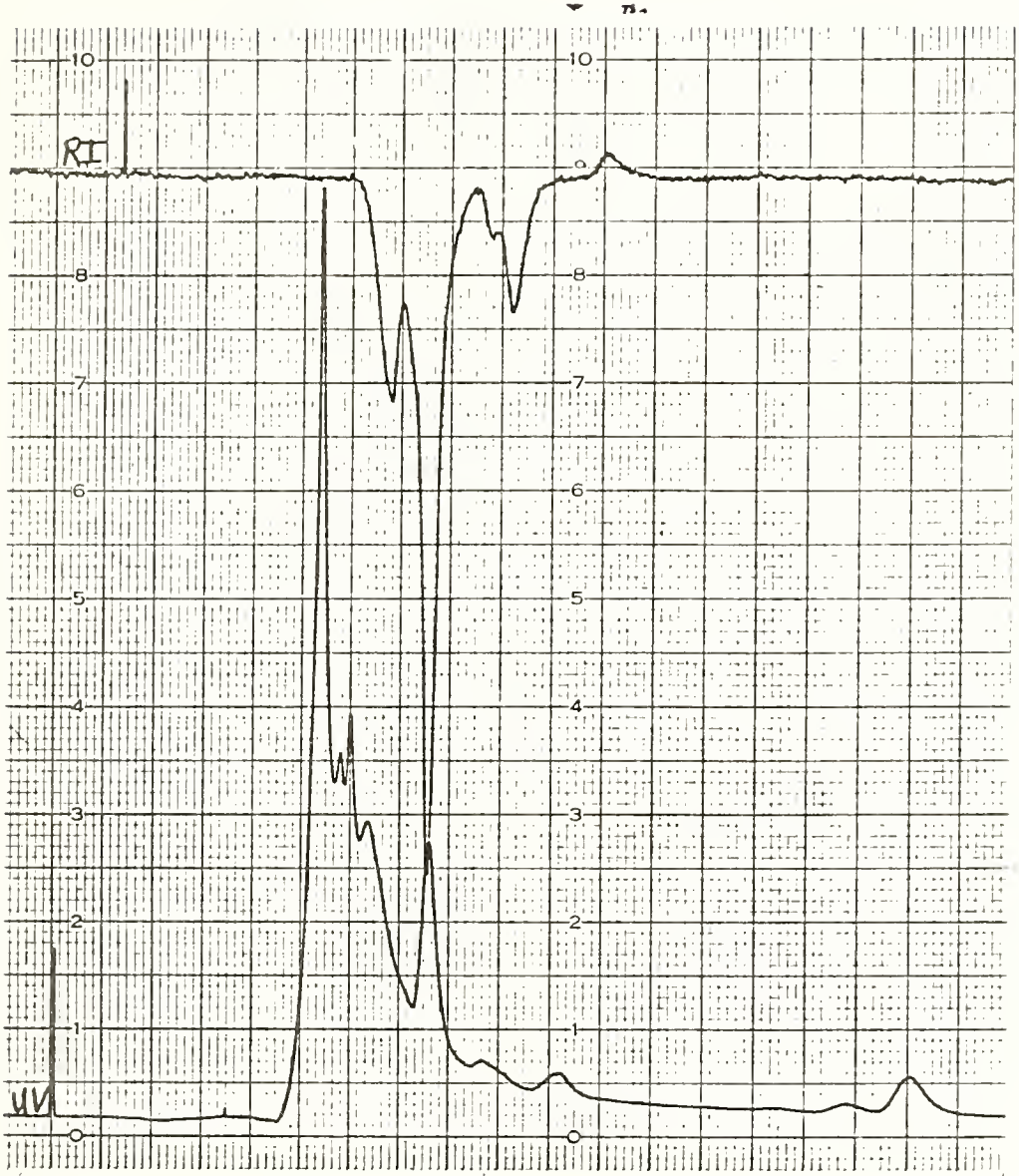
Nibe CHART TYPE EC 146 HOUSTON INSTRUMENT

Figure - 22



ADMIXTURE: C
Mobile Phase: 80/20 CH_3CN/H_2O
Flow Rate: 1.1 ml./min.
Column: LiChrosorb RP-18,10u
Injection Vol.: 10ul
UV Sensitivity: 0.05
RI Sensitivity: 4x
Chart Speed: 1 in./min.

Figure - 23



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Mobile Phase: 80/20 CH_3CN/H_2O
Flow Rate: 1.1 ml./min.
Column: LiChrosorb RP-18,10u
Injection Vol.: 10ul
UV Sensitivity: 0.05
RI Sensitivity: 4x
Chart Speed: 1 in./min.

Figure - 24

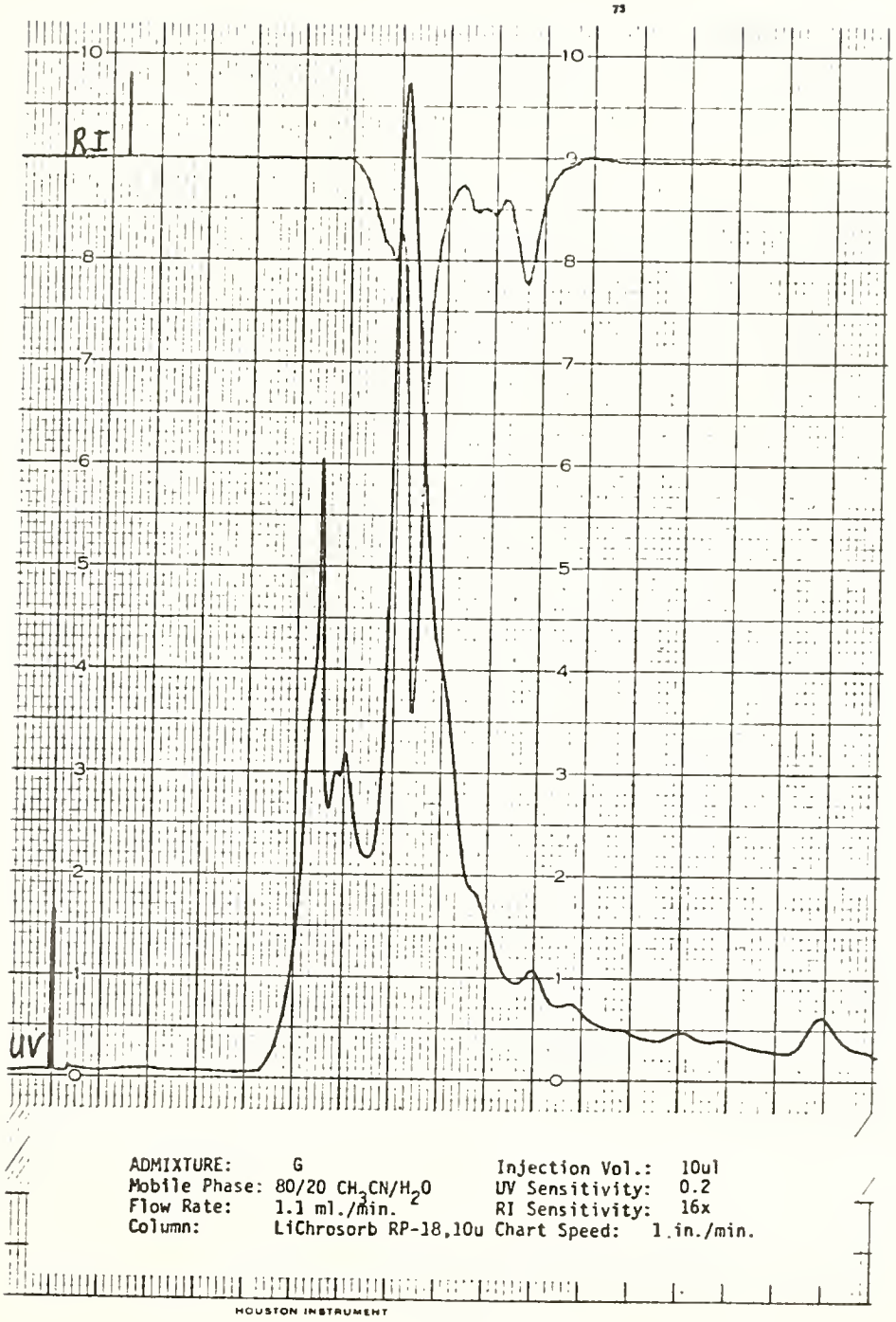
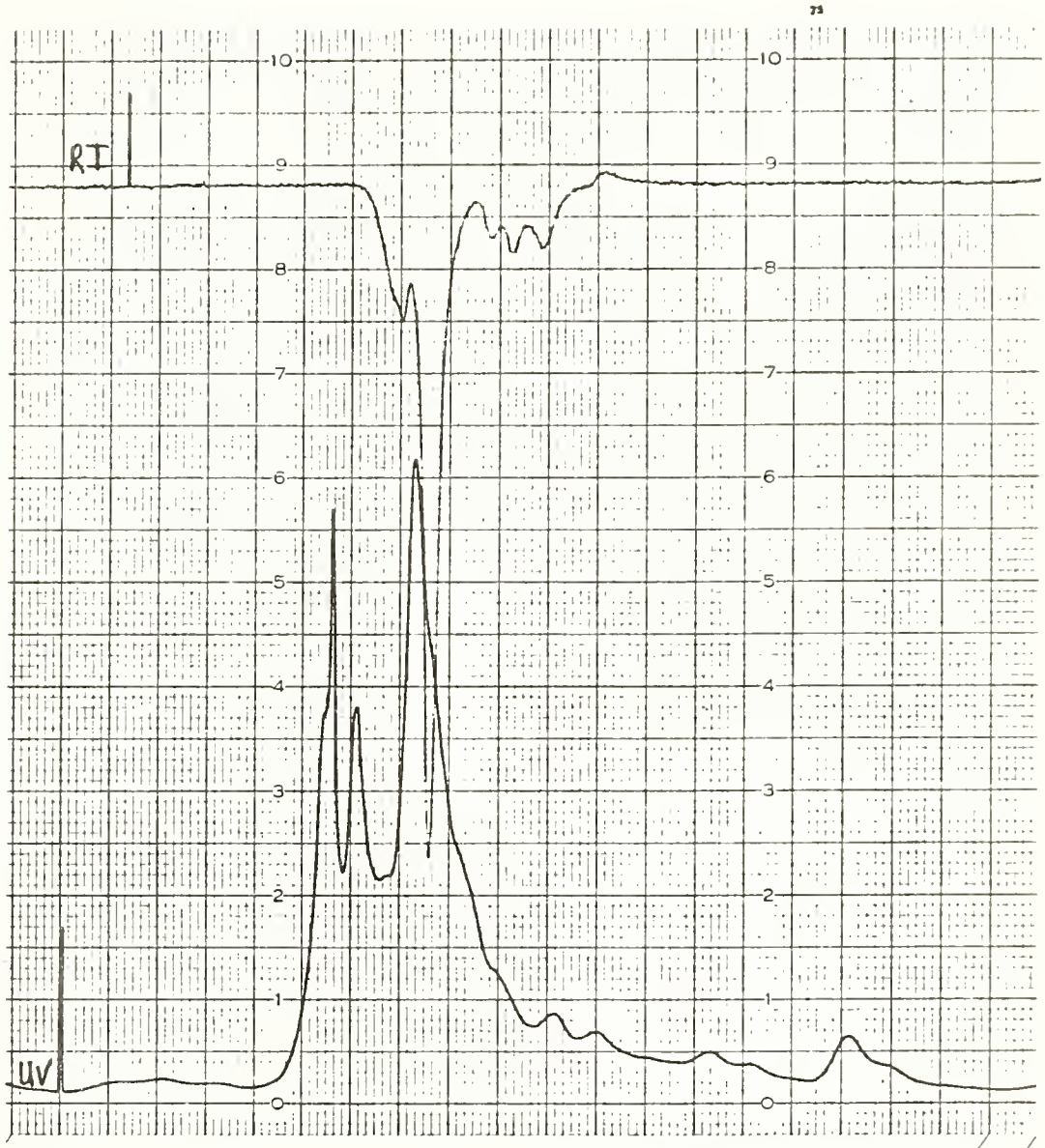

RI
uv
ADMIXTURE: G
Mobile Phase: 80/20 CH3CN/H2O
Flow Rate: 1.1 ml./min.
Column: LiChrosorb RP-18,10u
Injection Vol.: 10ul
UV Sensitivity: 0.2
RI Sensitivity: 16x
Chart Speed: 1 in./min.
HOUSTON INSTRUMENT

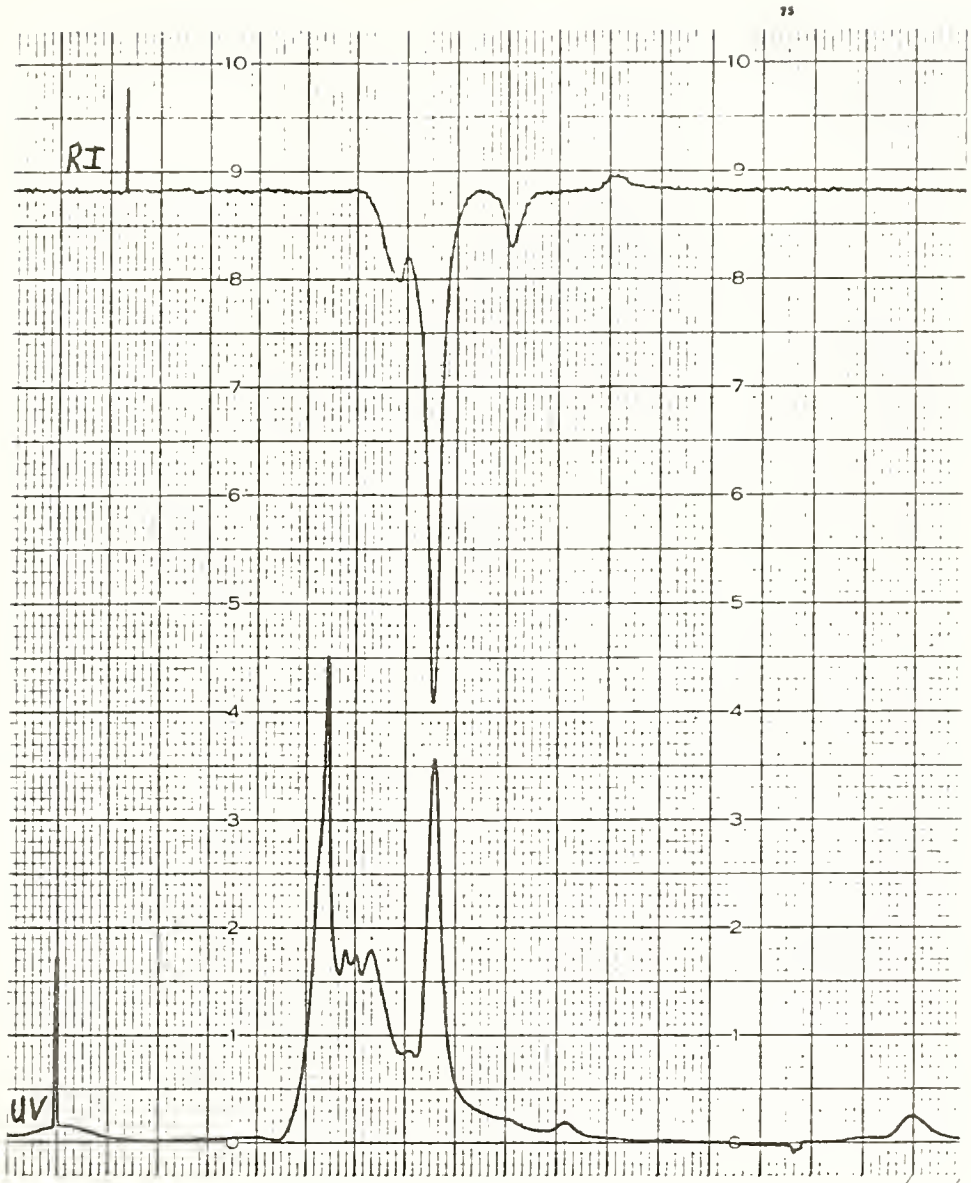
Figure - 25



ADMIXTURE: H
Mobile Phase: 80/20 CH_3CN/H_2O
Flow Rate: 1.1 ml./min.
Column: LiChrosorb RP-18,10u
Injection Vol.: 10ul
UV Sensitivity: 0.1
RI Sensitivity: 8x
Chart Speed: 1 in./min.

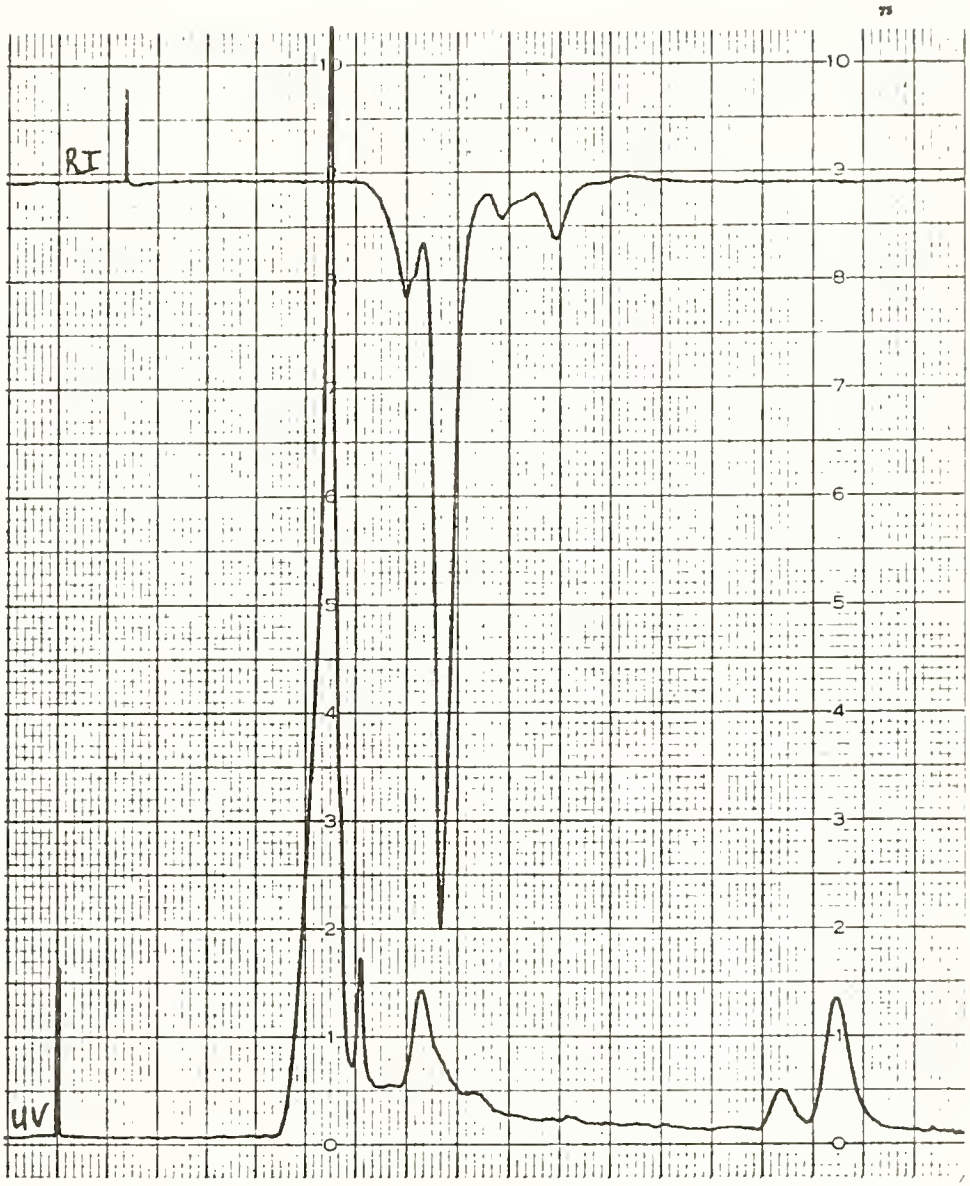
CHART TYPE EC 146 HOUSTON INSTRUMENT

Figure - 26



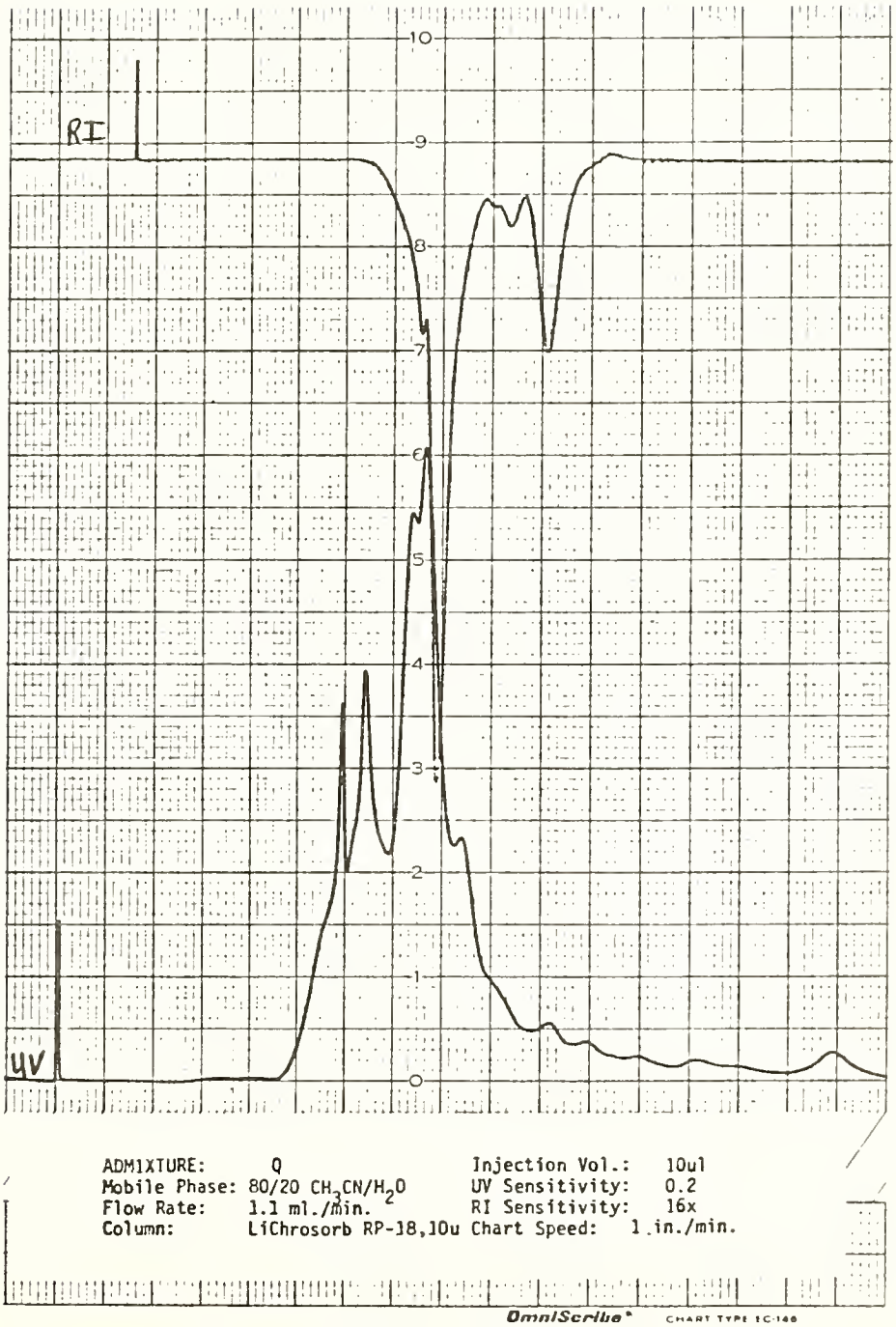
ADMIXTURE: I
Mobile Phase: 80/20 CH_3CN/H_2O
Flow Rate: 1.1 ml./min.
Column: LiChrosorb RP-18,10u
Injection Vol.: 10ul
UV Sensitivity: 0.1
RI Sensitivity: 8x
Chart Speed: 1 in./min.

Figure - 27



ADMIXTURE: P
Mobile Phase: 80/20 CH_3CN/H_2O
Flow Rate: 1.1 ml./min.
Column: LiChrosorb RP-18,10u
Injection Vol.: 10ul
UV Sensitivity: 0.5
RI Sensitivity: 16x
Chart Speed: 1 in./min.

Figure - 28


RI
UV
10
9
8
7
6
5
4
3
2
1
0
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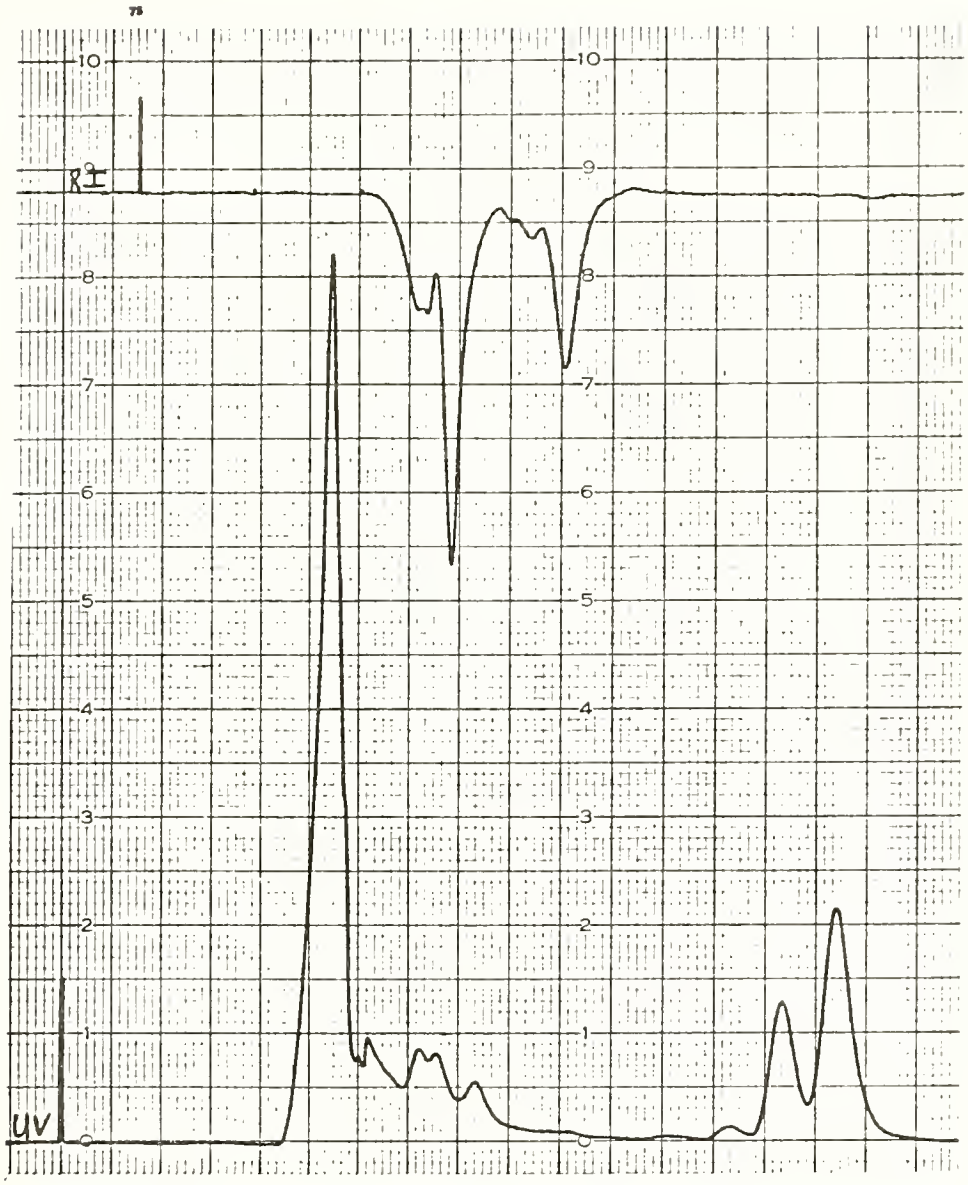
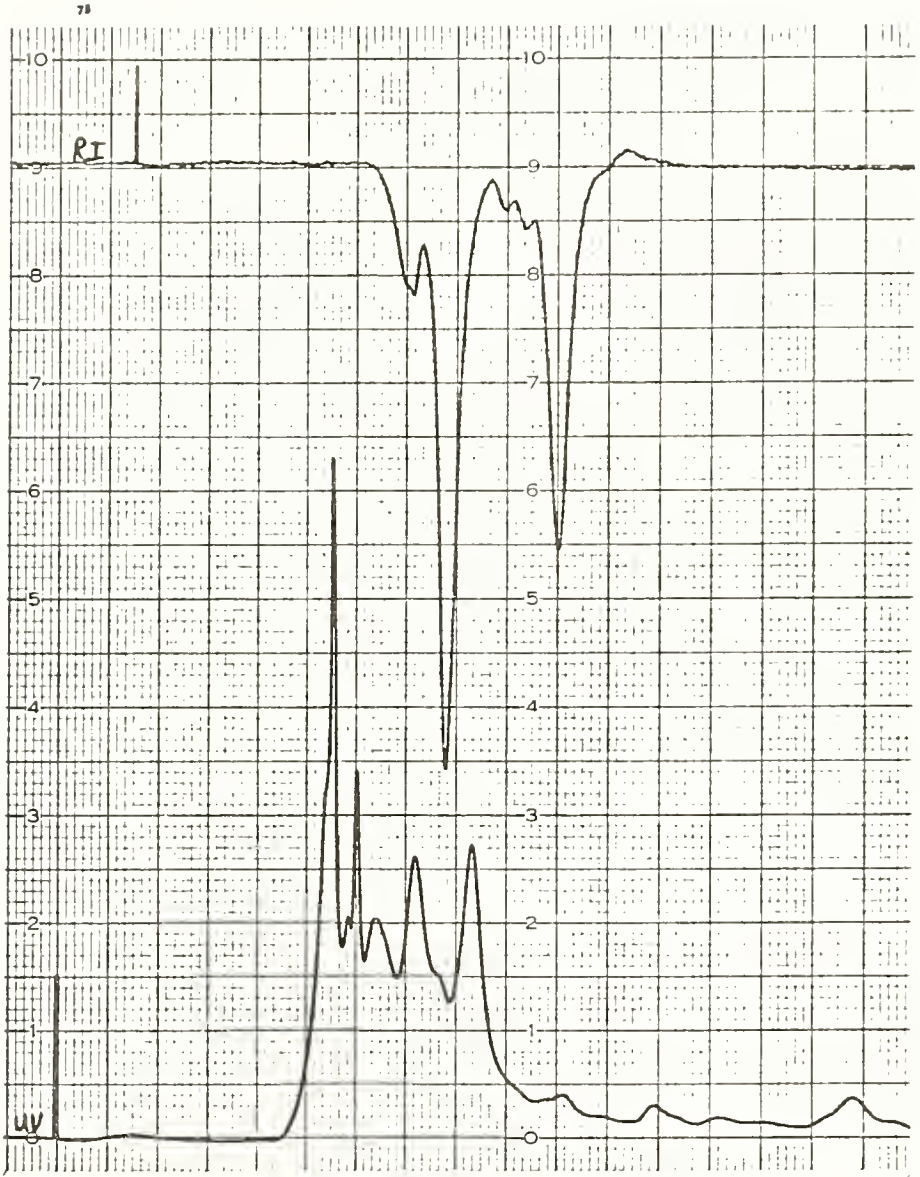
Mobile Phase: 80/20 CH_3CN/H_2O
Flow Rate: 1.1 ml./min.
Column: LiChrosorb RP-18,10u
Injection Vol.: 10ul
UV Sensitivity: 0.2
RI Sensitivity: 16x
Chart Speed: 1 in./min.
OmniScribe® CHART TYPE SC-146

Figure - 29



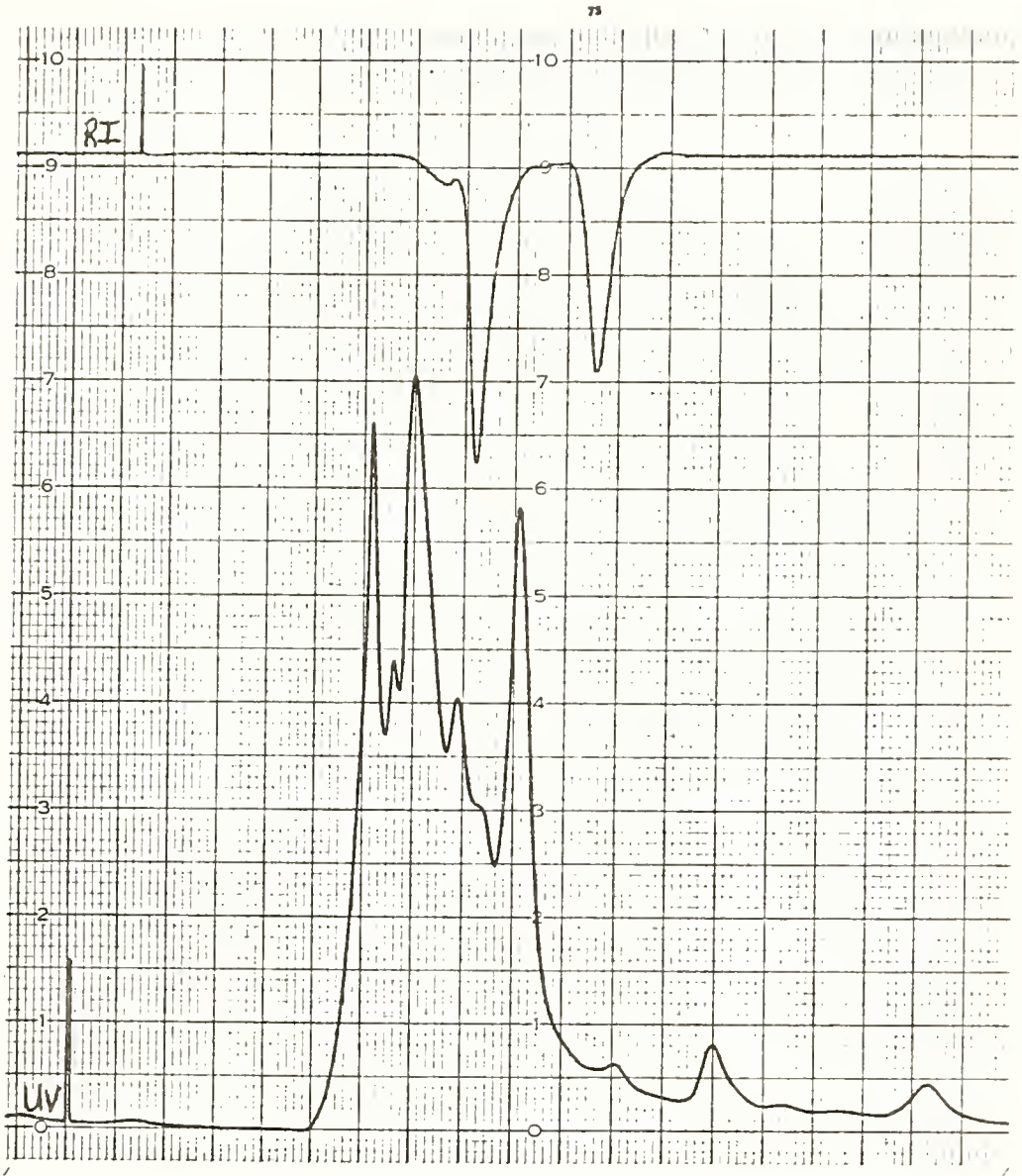
ADMIXTURE: R
Mobile Phase: 80/20 CH_3CN/H_2O
Flow Rate: 1.1 ml./min.
Column: LiChrosorb RP-18,10u
Injection Vol.: 10ul
UV Sensitivity: 0.5
RI Sensitivity: 16x
Chart Speed: 1 in./min.

Figure - 30



ADMIXTURE: S
Mobile Phase: 80/20 CH_3CN/H_2O
Flow Rate: 1.1 ml./min.
Column: LiChrosorb RP-18,10u
Injection Vol.: 10ul
UV Sensitivity: 0.1
RI Sensitivity: 8x
Chart Speed: 1 in./min.

Figure - 31



ADMIXTURE: T
Mobile Phase: 80/20 CH_3CN/H_2O
Flow Rate: 1.1 ml./min.
Column: LiChrosorb RP-18,10u
Injection Vol.: 10ul
UV Sensitivity: 0.1
RI Sensitivity: 16x
Chart Speed: 1 in./min.

Figure - 32

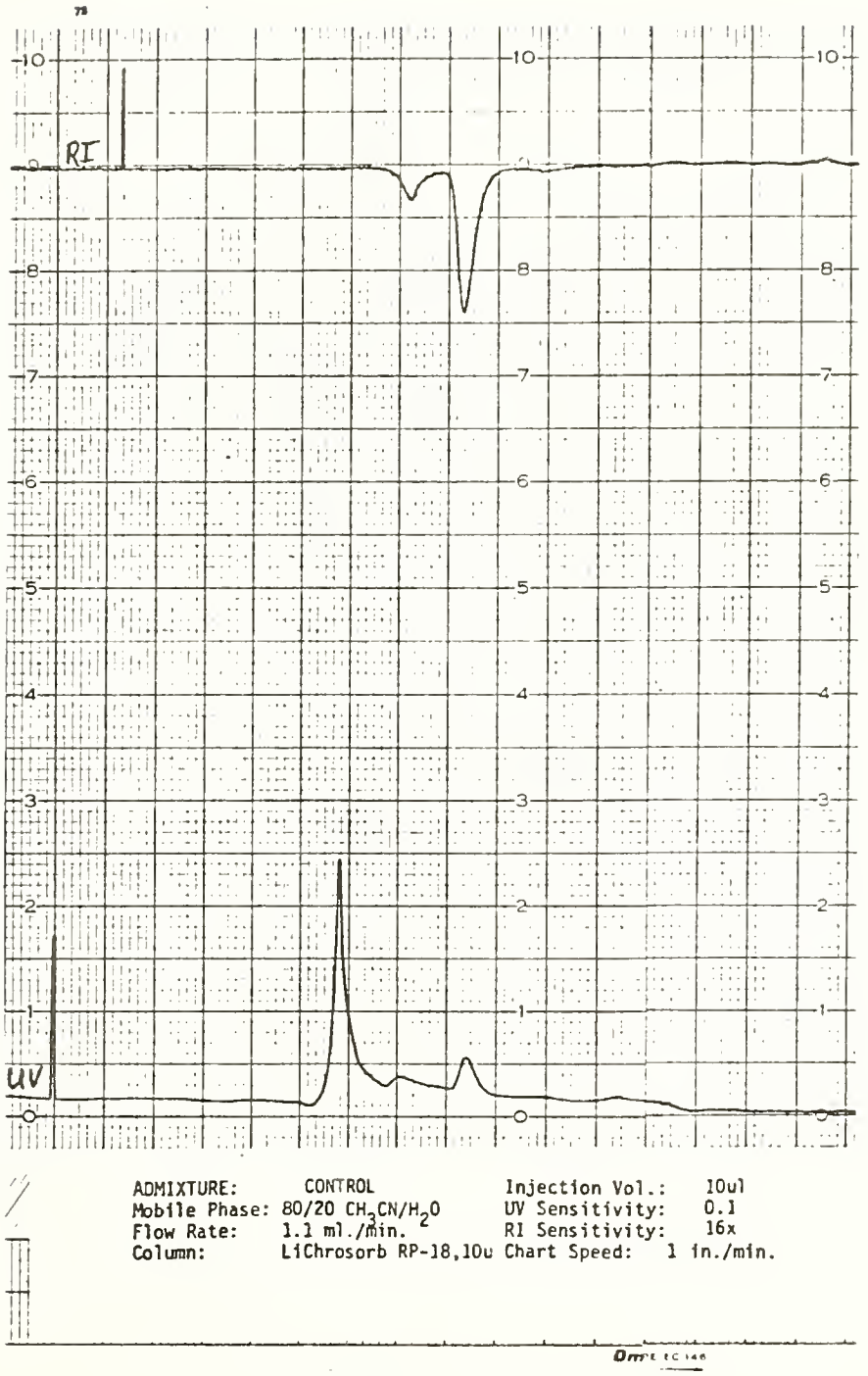
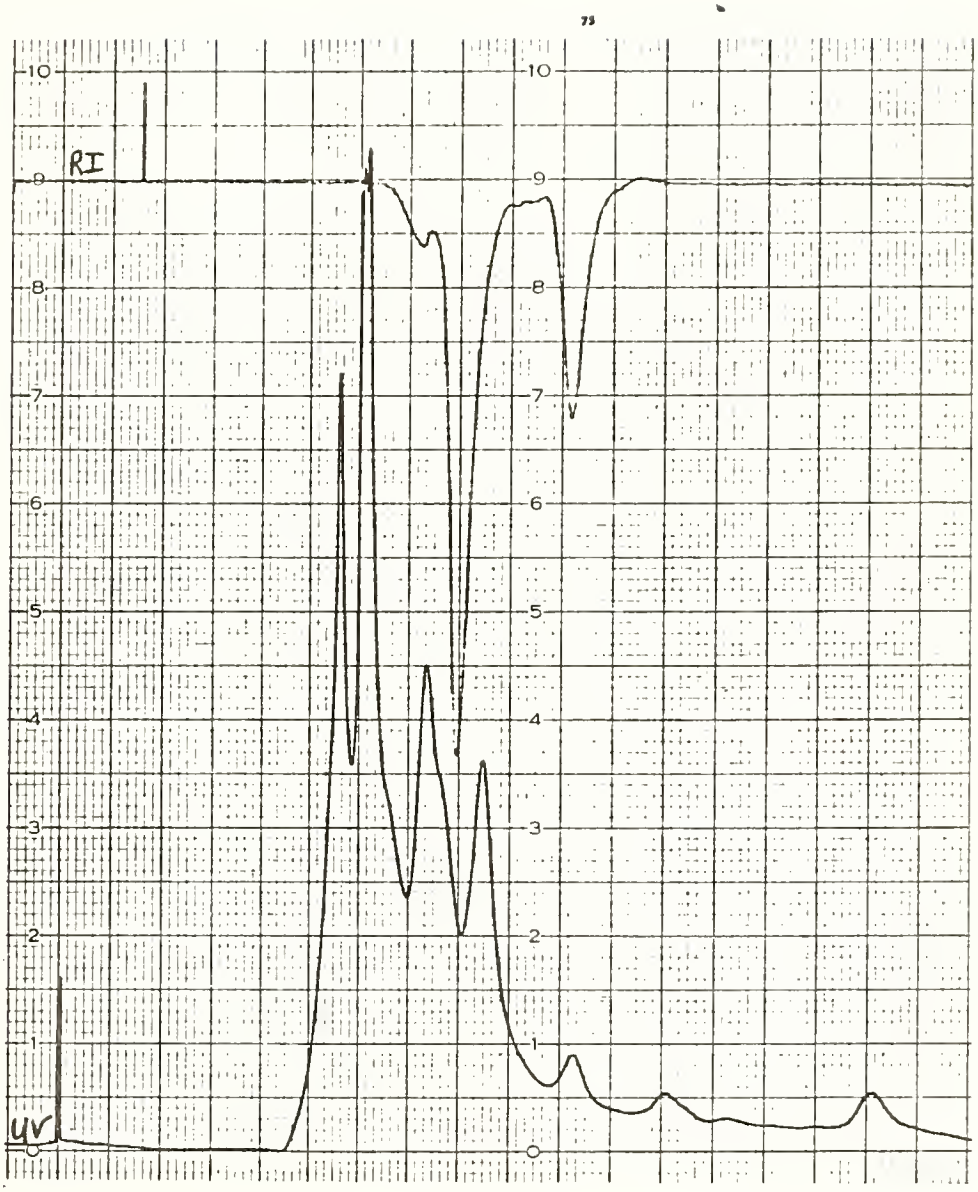

RI
UV
ADMIXTURE: CONTROL
Mobile Phase: 80/20 CH_3CN/H_2O
Flow Rate: 1.1 ml./min.
Column: LiChrosorb RP-18,10u
Injection Vol.: 10ul
UV Sensitivity: 0.1
RI Sensitivity: 16x
Chart Speed: 1 in./min.

Figure - 33

Part 2.



ADMIXTURE: A-B
Mobile Phase: 80/20 CH_3CN/H_2O
Flow Rate: 1.1 ml./min.
Column: LiChrosorb RP-18,10u
Injection Vol.: 10ul
UV Sensitivity: 0.05
RI Sensitivity: 8x
Chart Speed: 1 in./min.

Figure - 34

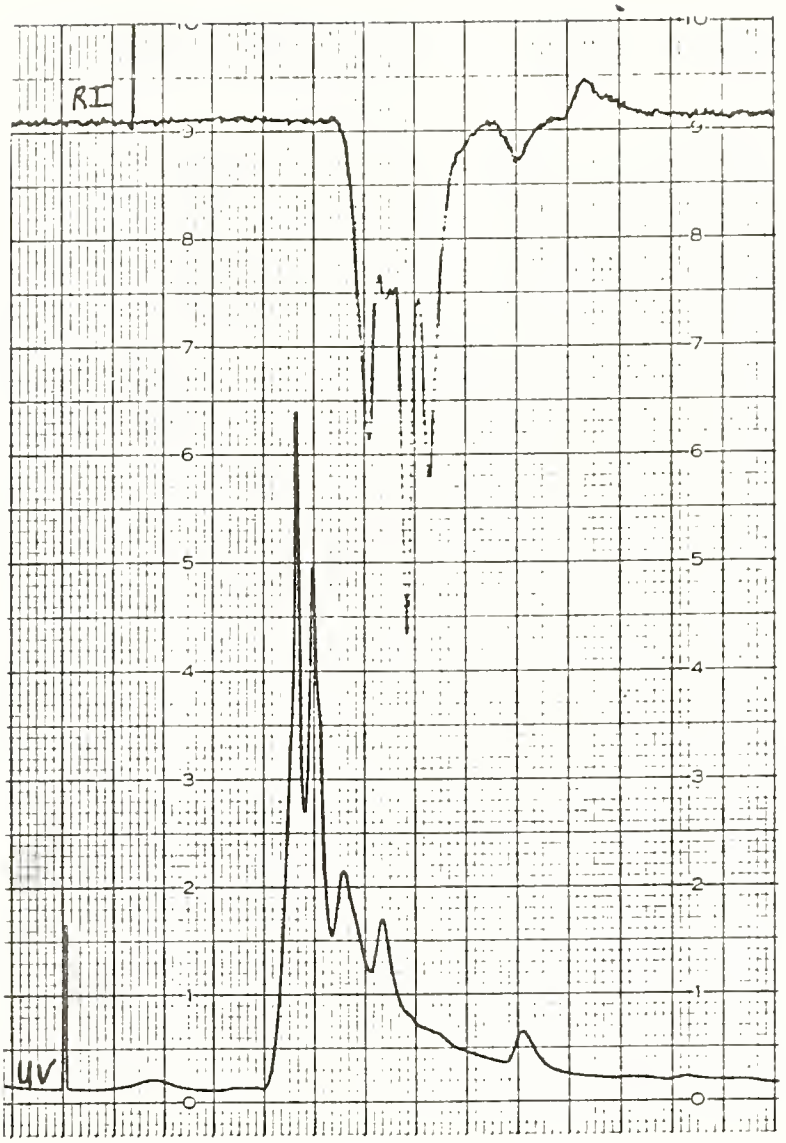
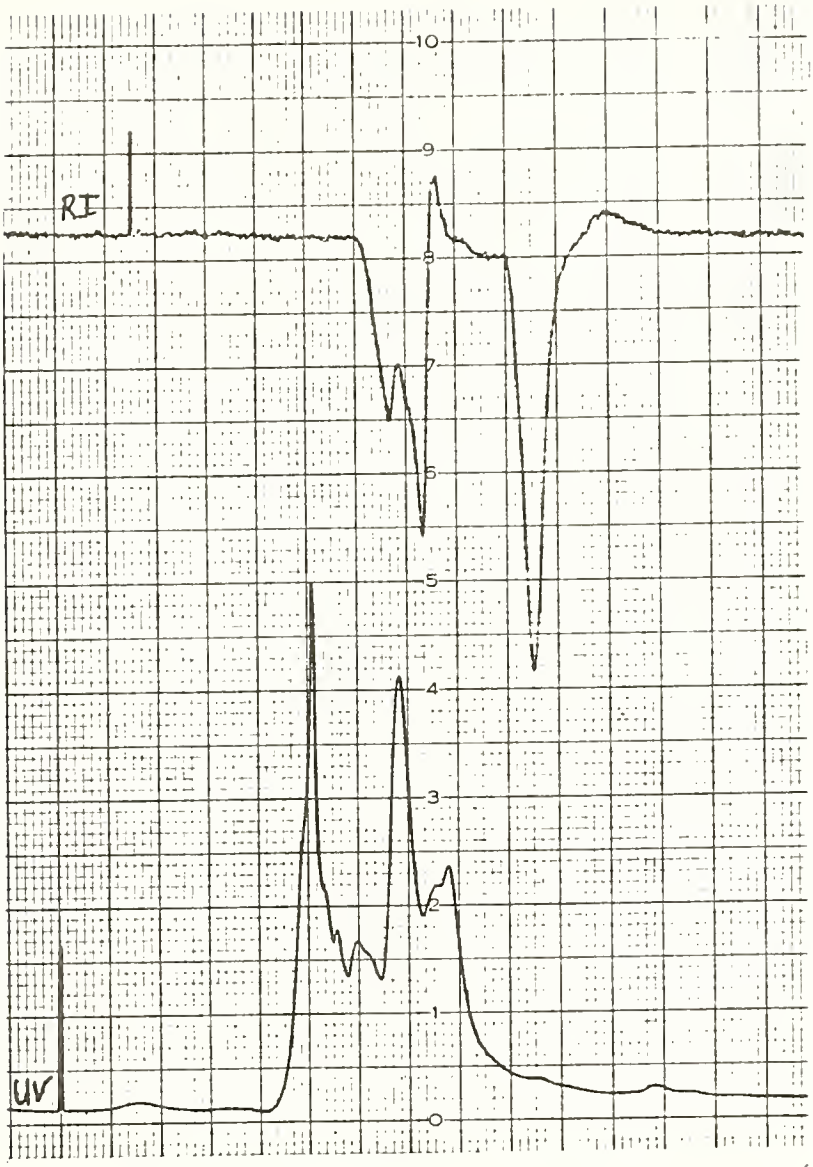

RI
UV
ADMIXTURE: K-L
Mobile Phase: 80/20 CH_3CN/H_2O
Flow Rate: 1.1 ml./min.
Column: LiChrosorb RP-18,10u
Injection Vol.: 10ul
UV Sensitivity: 0.1
RI Sensitivity: 8x
Chart Speed: 1 in./min.

Figure - 35



ADMIXTURE: D-E
Mobile Phase: 80/20 CH_3CN/H_2O
Flow Rate: 1.1 ml./min.
Column: LiChrosorb RP-18,10u
Injection Vol.: 10ul
UV Sensitivity: 0.1
RI Sensitivity: 8x
Chart Speed: 1 in./min.

Figure - 36

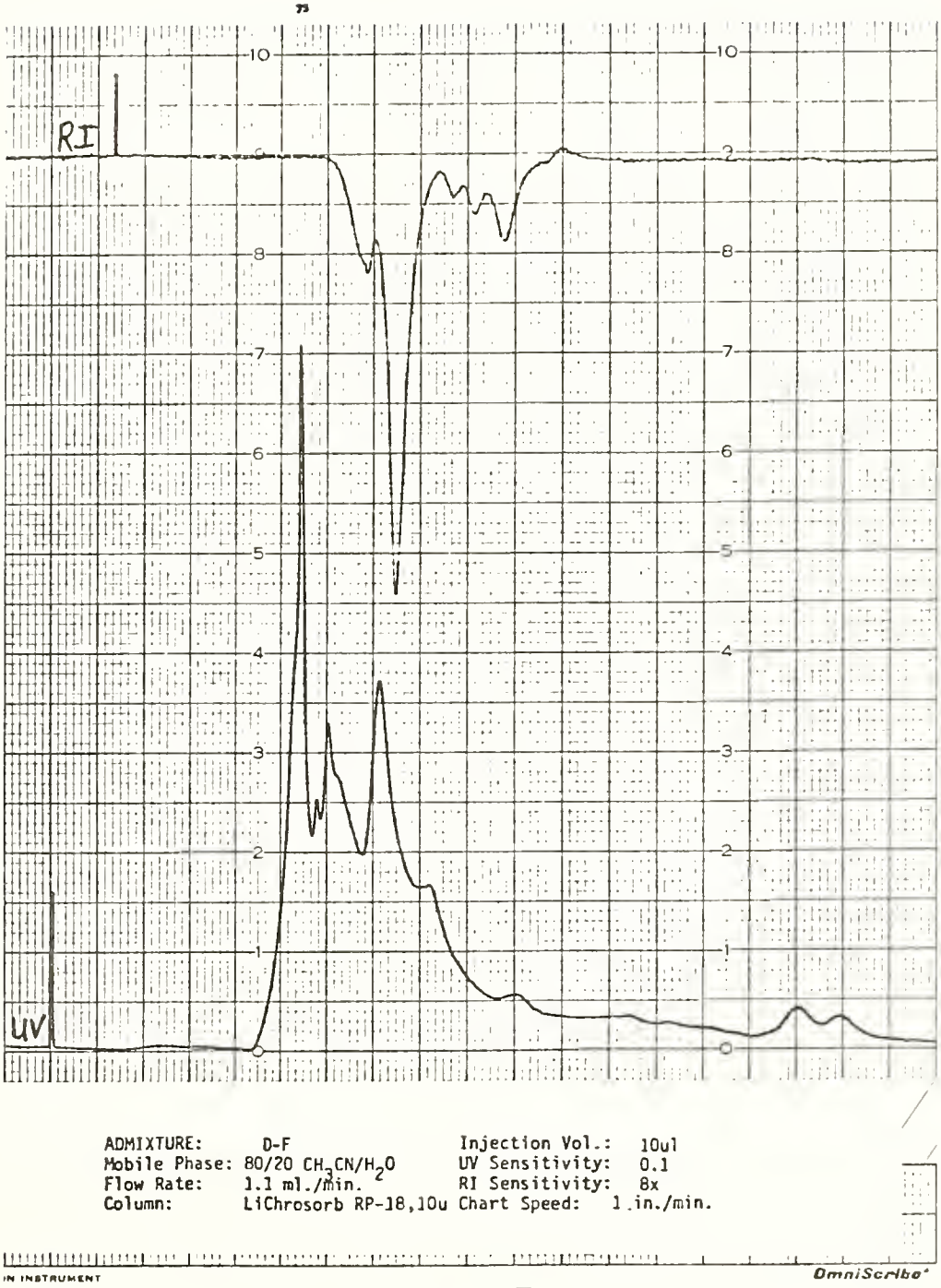
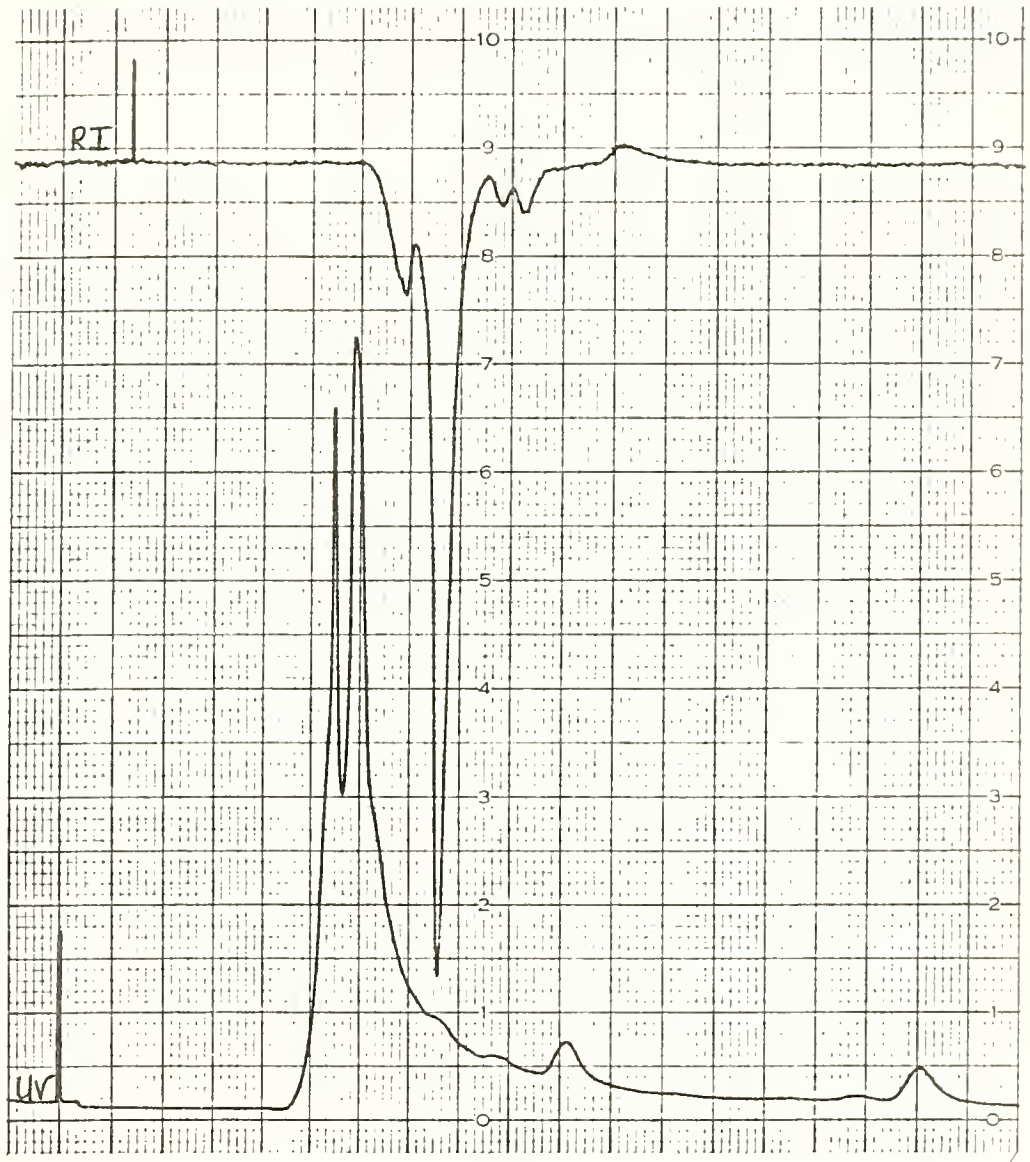

RI
UV
10
8
7
6
5
4
3
2
1
0
ADMIXTURE: D-F
Mobile Phase: 80/20 CH_3CN/H_2O
Flow Rate: 1.1 ml./min.
Column: LiChrosorb RP-18,10u
Injection Vol.: 10ul
UV Sensitivity: 0.1
RI Sensitivity: 8x
Chart Speed: 1 in./min.
IN INSTRUMENT
OmniScribe

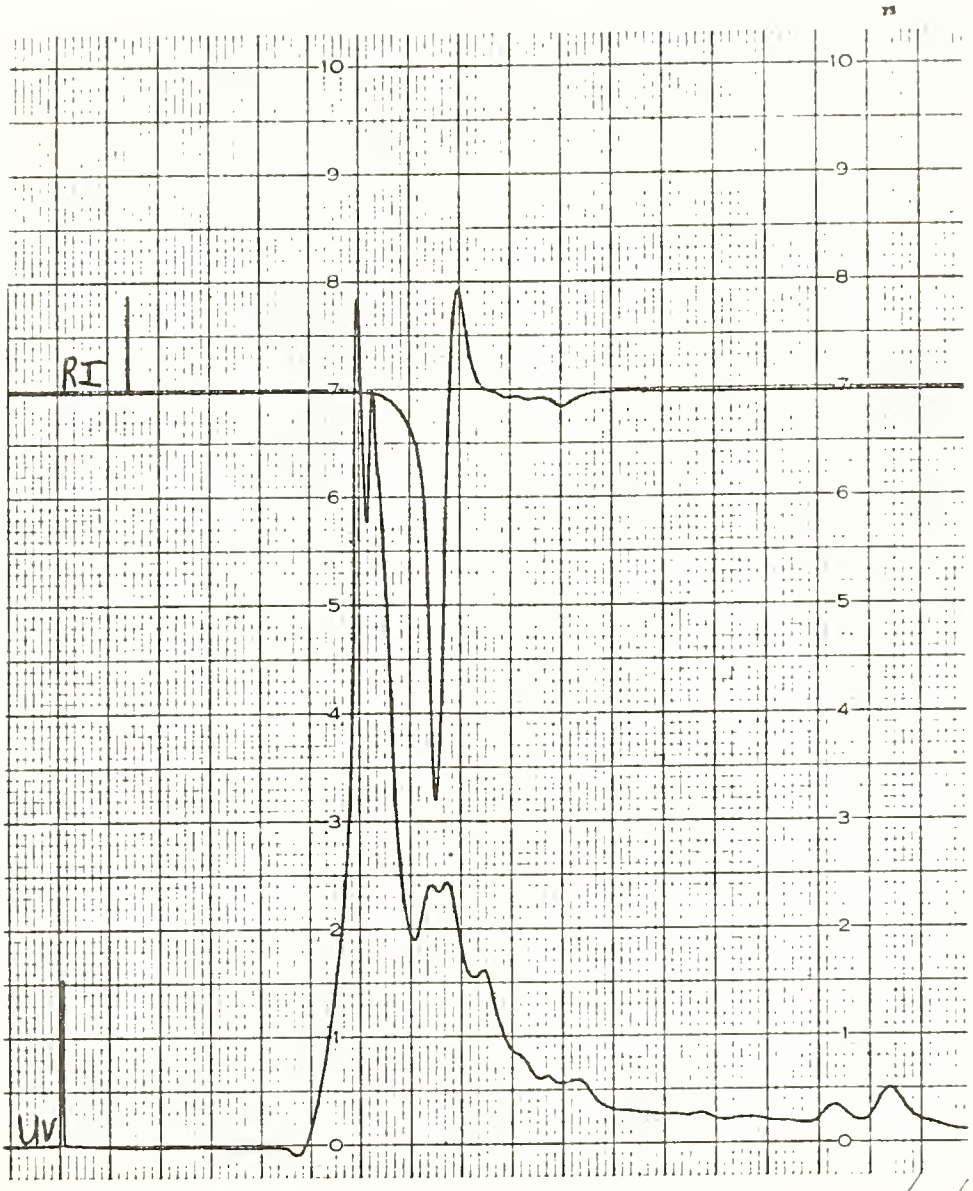
Figure - 37



ADMIXTURE: K-M
Mobile Phase: 80/20 CH_3CN/H_2O
Flow Rate: 1.1 ml./min.
Column: LiChrosorb RP-18,10u
Injection Vol.: 10ul
UV Sensitivity: 0.1
RI Sensitivity: 8x
Chart Speed: 1 in./min.

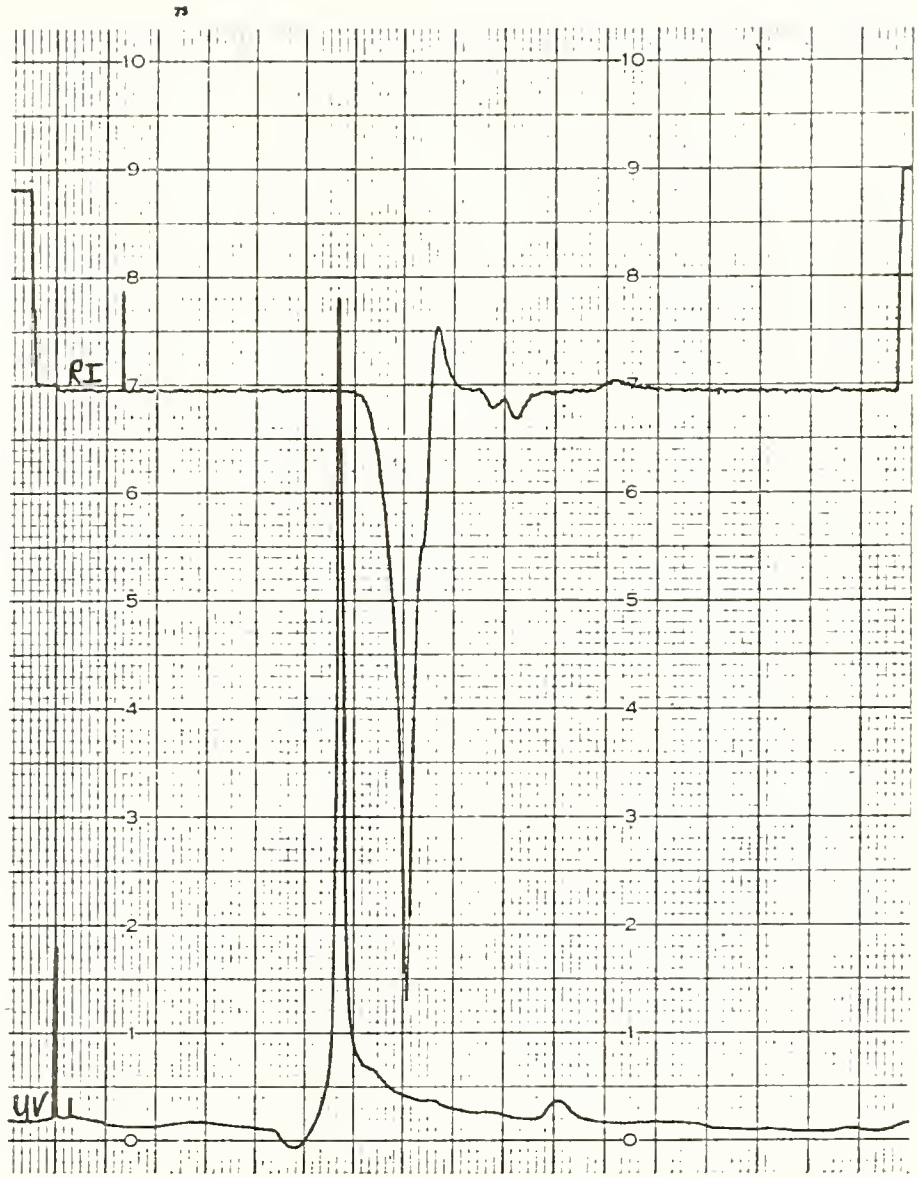
OmniScribe® CHART TYPE EC 146 HOUSTON INSTRUMENT

Figure - 38



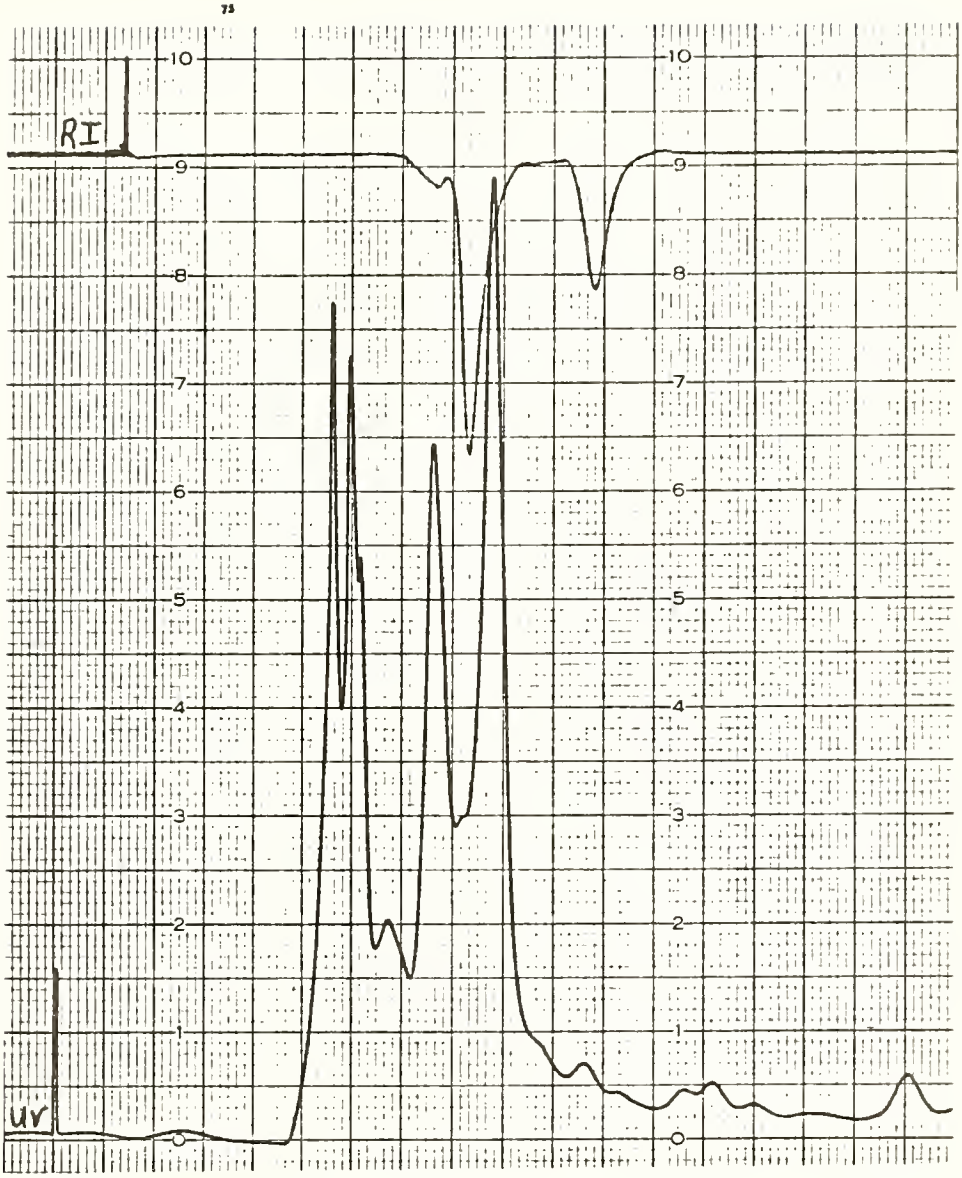
ADMIXTURE: D-J
Mobile Phase: 80/20 CH_3CN/H_2O
Flow Rate: 1.1 ml./min.
Column: LiChrosorb RP-18,10u
Injection Vol.: 10ul
UV Sensitivity: 0.1
RI Sensitivity: 64x
Chart Speed: 1 in./min.

Figure - 39



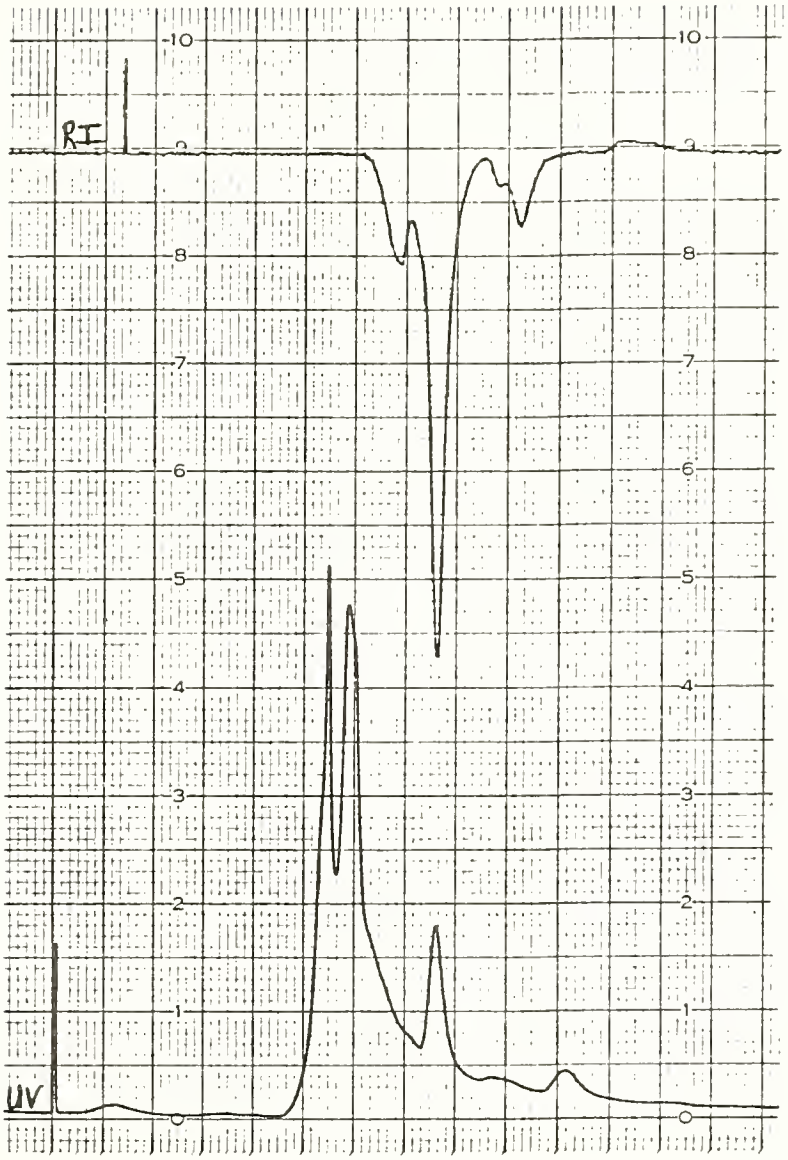
ADMIXTURE: K-N
Mobile Phase: 80/20 CH_3CN/H_2O
Flow Rate: 1.1 ml./min.
Column: LiChrosorb RP-18,10u
Injection Vol.: 5ul
UV Sensitivity: 0.1
RI Sensitivity: 8x
Chart Speed: 1 in./min.

Figure - 40



ADMIXTURE: A-C
Mobile Phase: 80/20 CH_3CN/H_2O
Flow Rate: 1.1 ml./min.
Column: LiChrosorb RP-18,10u
Injection Vol.: 5ul
UV Sensitivity: 0.1
RI Sensitivity: 8x
Chart Speed: 1 in./min.

Figure - 41



ADMIXTURE: K-0
Mobile Phase: 80/20 CH_3CN/H_2O
Flow Rate: 1.1 ml./min.
Column: LiChrosorb RP-18,10u
Injection Vol.: 10ul
UV Sensitivity: 0.1
RI Sensitivity: 8x
Chart Speed: 1 in./min.

UmniScribe CHART TYPE EC 146

Figure - 42

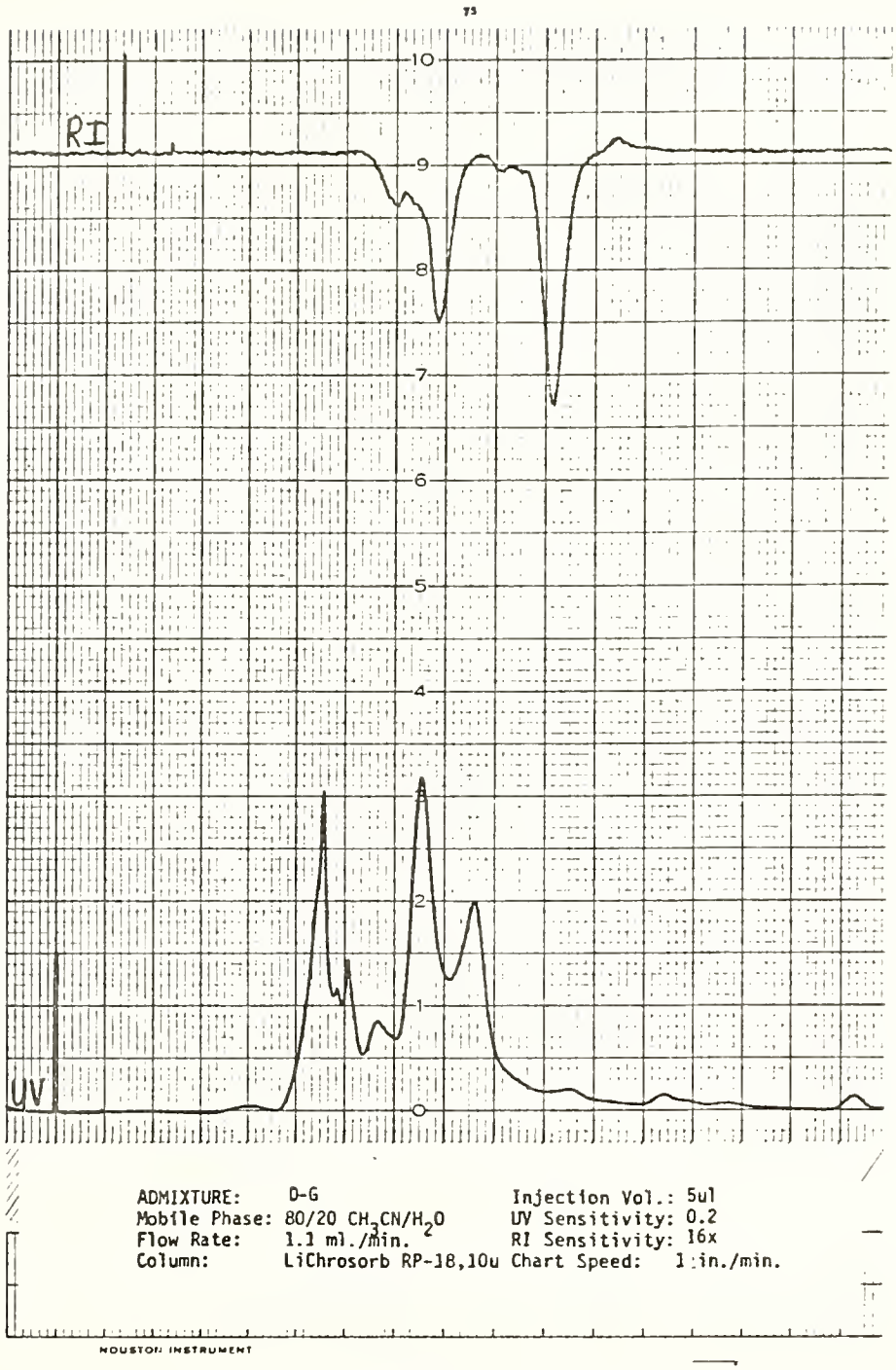
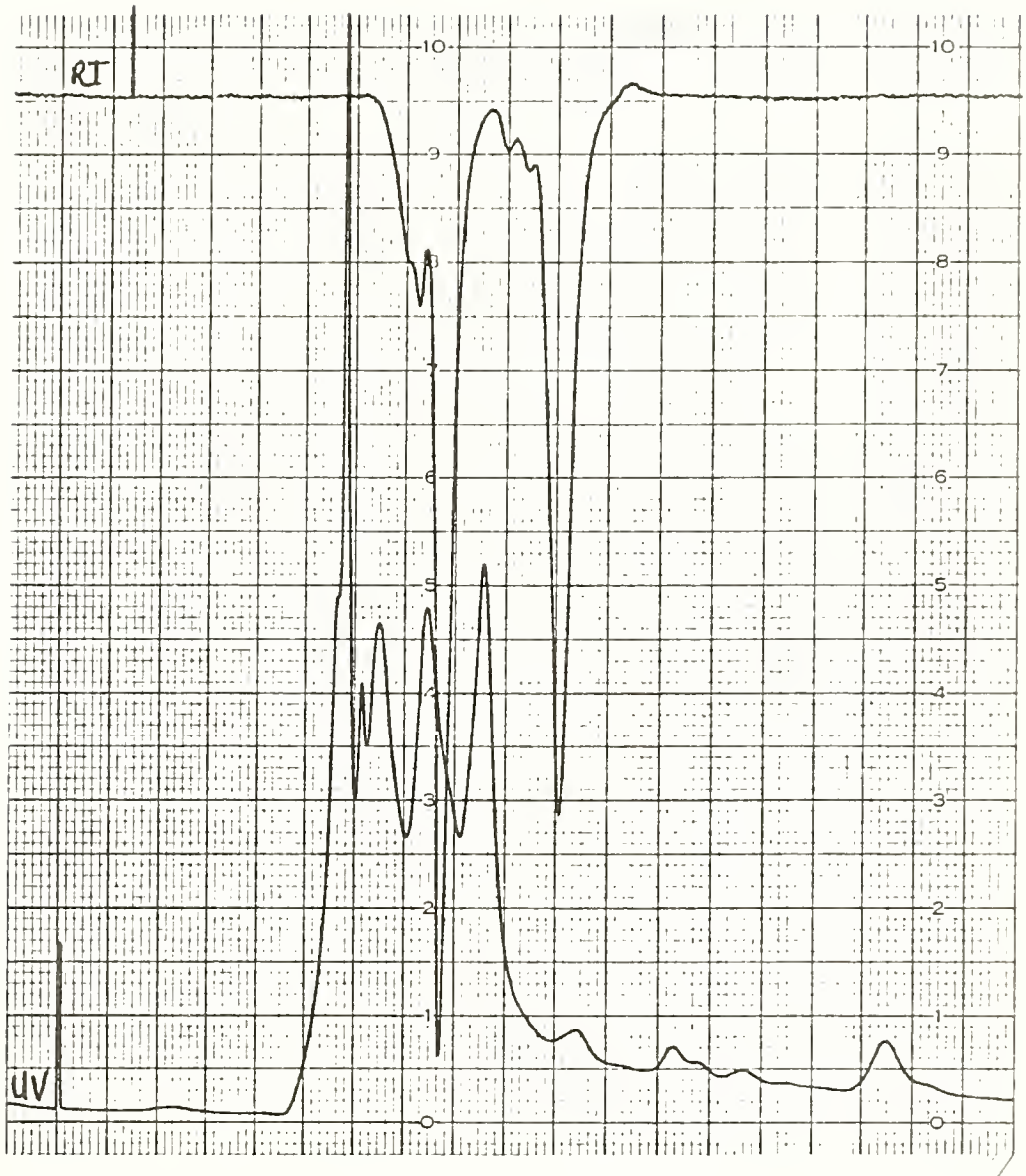

RI
UV
10
9
8
7
6
5
4
3
2
1
0
ADMIXTURE: D-G
Mobile Phase: 80/20 CH_3CN/H_2O
Flow Rate: 1.1 ml./min.
Column: LiChrosorb RP-18,10u
Injection Vol.: 5ul
UV Sensitivity: 0.2
RI Sensitivity: 16x
Chart Speed: 1 in./min.
HOUSTON INSTRUMENT

Figure - 43


RI
UV
10
9
8
7
6
5
4
3
2
1
0
ADMIXTURE: D-H
Mobile Phase: 80/20 CH_3CN/H_2O
Flow Rate: 1.1 ml./min.
Column: LiChrosorb RP-18,10u
Injection Vol.: 10ul
UV Sensitivity: 0.1
RI Sensitivity: 8x
Chart Speed: 1 in./min.

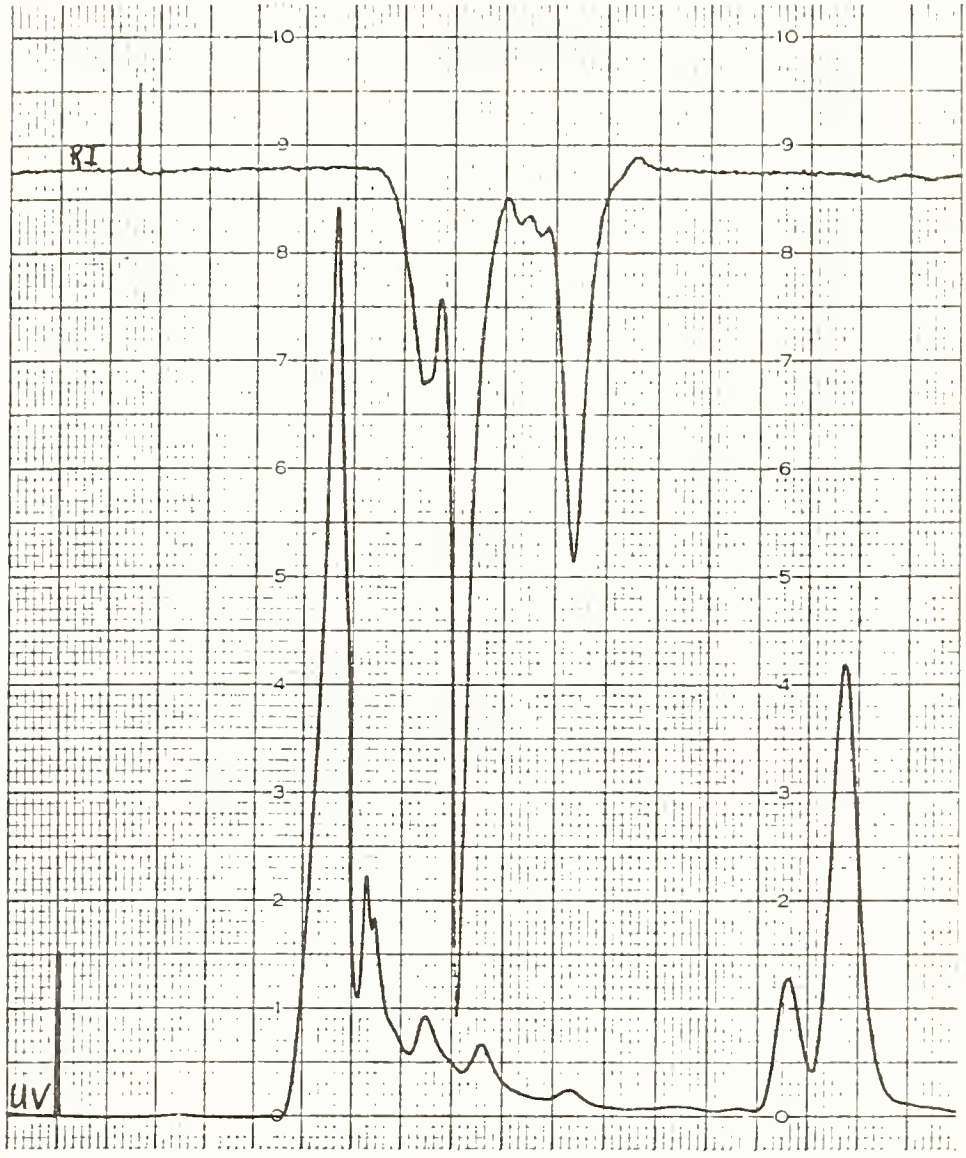
Figure - 44



ADMIXTURE: D-I
Mobile Phase: 80/20 CH_3CN/H_2O
Flow Rate: 1.1 ml./min.
Column: LiChrosorb RP-18,10u
Injection Vol.: 10ul
UV Sensitivity: 0.1
RI Sensitivity: 8x
Chart Speed: 1 in./min.

OmniScribe CHART TYPE SC 146

Figure - 45



ADMIXTURE: K-P
Mobile Phase: 80/20 CH_3CN/H_2O
Flow Rate: 1.1 ml./min.
Column: LiChrosorb RP-18,10u
Injection Vol.: 10ul
UV Sensitivity: 0.5
RI Sensitivity: 8x
Chart Speed: 1 in./min.

Figure - 46

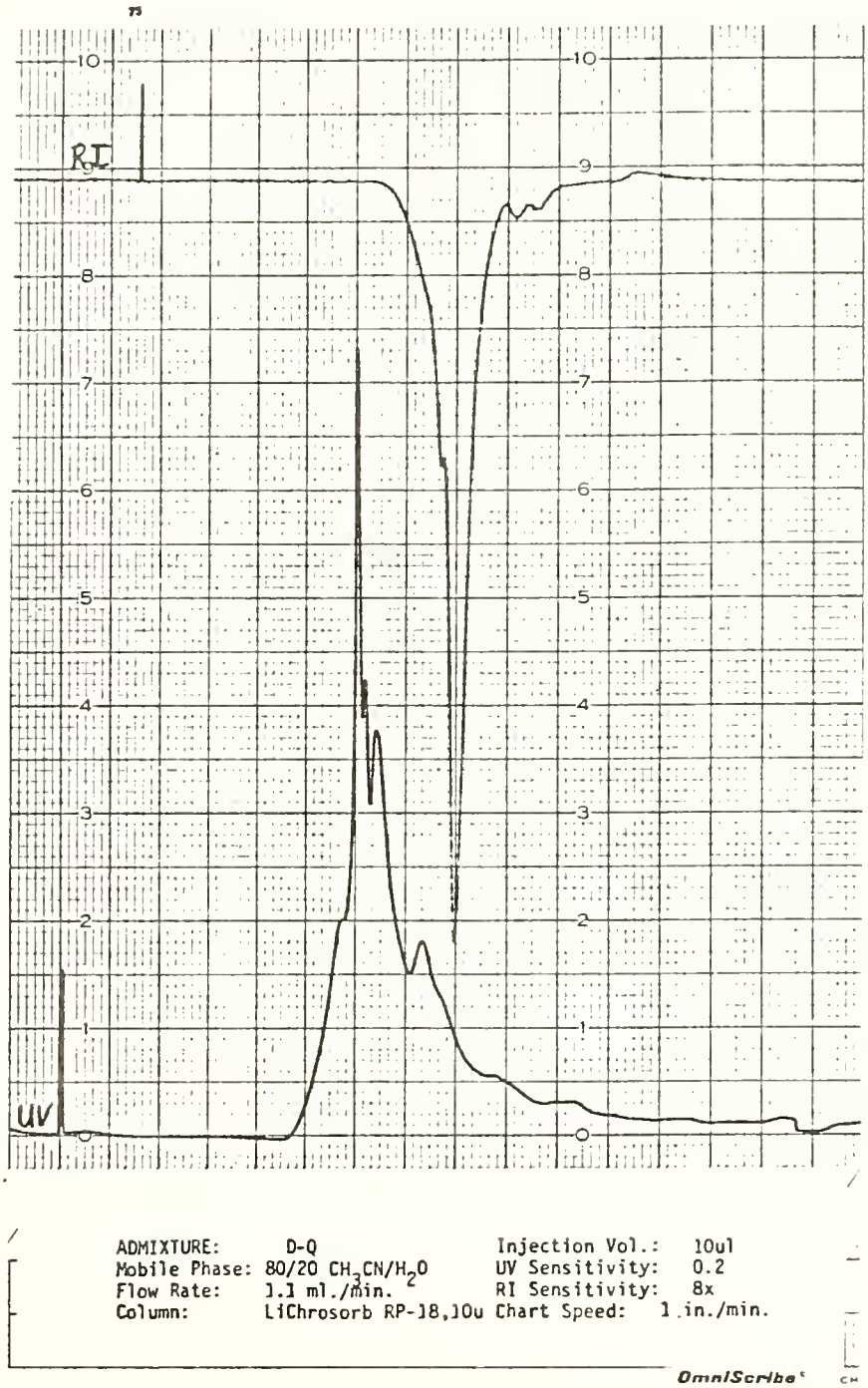
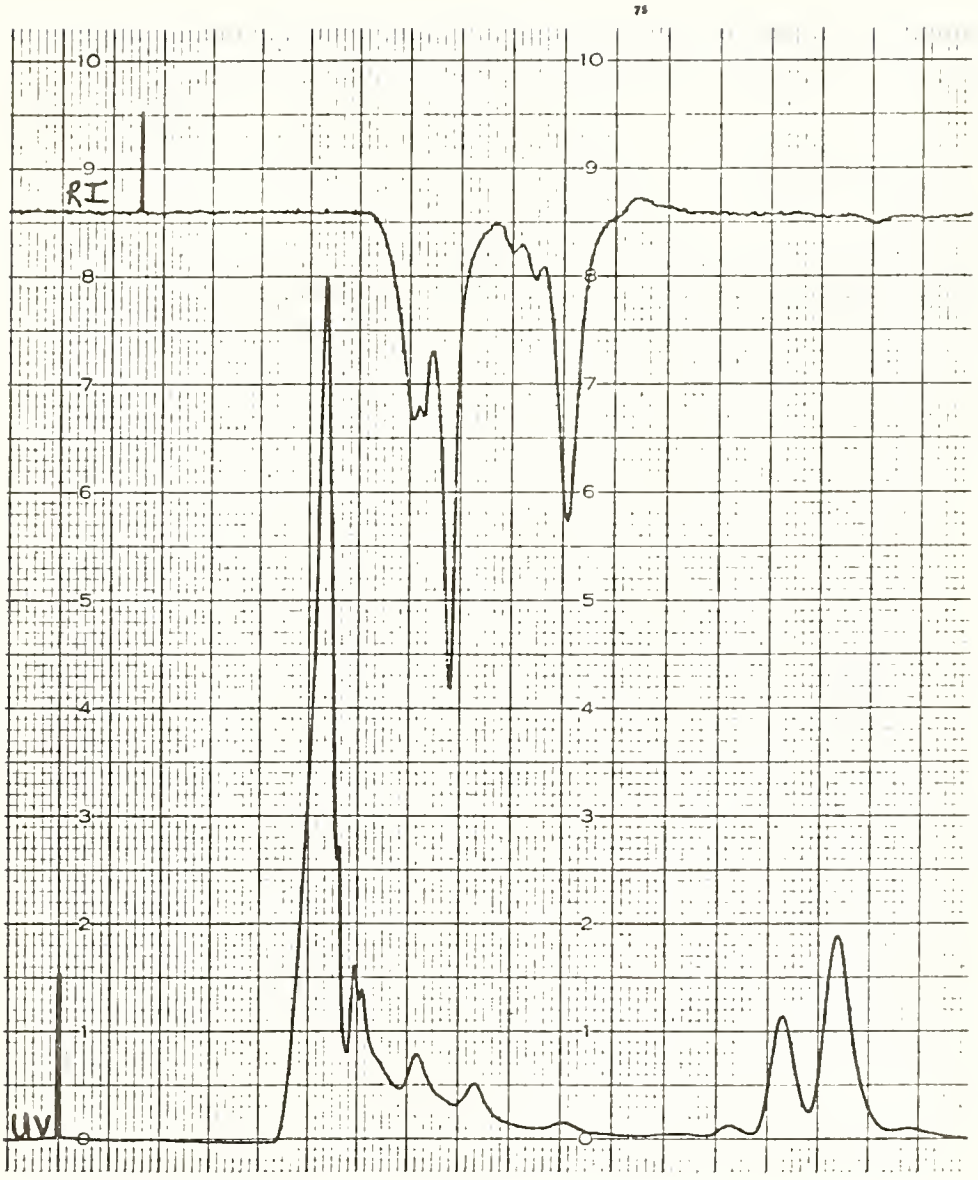
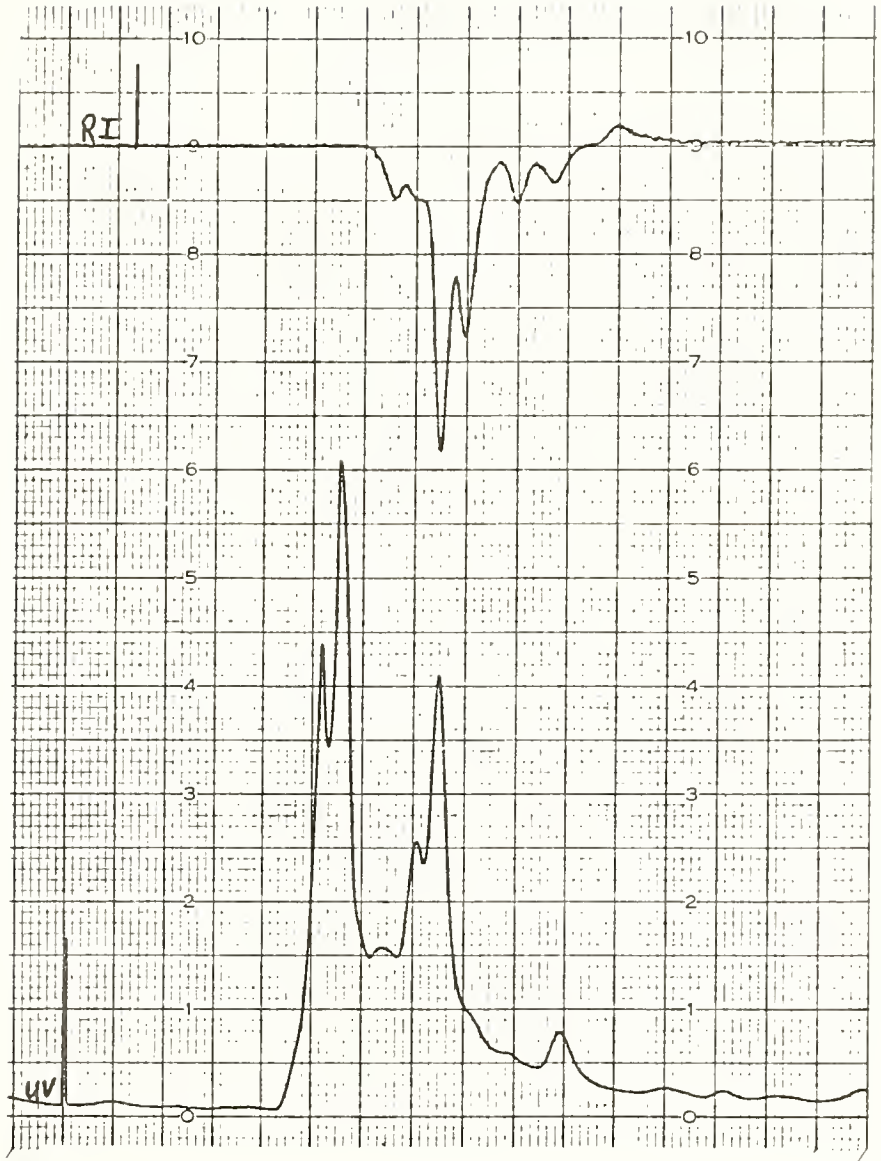

RI
UV
10
9
8
7
6
5
4
3
2
1
0
ADMIXTURE: D-Q
Mobile Phase: 80/20 CH_3CN/H_2O
Flow Rate: 1.1 ml./min.
Column: LiChrosorb RP-18,10u
Injection Vol.: 10ul
UV Sensitivity: 0.2
RI Sensitivity: 8x
Chart Speed: 1 in./min.
OmniScribe

Figure - 47



ADMIXTURE: A-R
Mobile Phase: 80/20 CH_3CN/H_2O
Flow Rate: 1.1 ml./min.
Column: LiChrosorb RP-18,10u
Injection Vol.: 10ul
UV Sensitivity: 0.5
RI Sensitivity: 8x
Chart Speed: 1 in./min.

Figure - 48



ADMIXTURE: K + O
Mobile Phase: 80/20 CH_3CN/H_2O
Flow Rate: 1.1 ml./min.
Column: LiChrosorb RP-18,10u
Injection Vol.: 10 ul
UV Sensitivity: 0.1
RI Sensitivity: 8x
Chart Speed: 1 in./min.

Figure - 49

CHAPTER VI - DISCUSSION

Extraction Methods

The purpose of this study was to develop an analytical scheme for the qualitative and semi-quantitative determination of the most common organic admixtures used in concrete. It was, therefore, necessary first to develop an efficient way to extract the organic material from the hardened concrete, and secondly to develop an analytical procedure using high pressure liquid chromatography for separating and identifying the materials in question.

Many solvents were used in attempting to extract the organic material from the hardened concrete or cement paste samples. Single solvents and solvent combinations, both binary and ternary azeotropes, differed in their selective interactions with various sample constituents. Chloroform, acetic acid, and water are strong proton-donor solvents that preferentially interact with hydrogen acceptor solutes, i.e. basic samples. Methanol, ethanol, and isopopanol are strong proton-acceptor solvents and interact preferentially with hydrogen-donor solutes, i.e. acidic samples. Methylethyl ketone (MEK), tetrahydrofuran, dioxane, and ethylene chloride are all solvents that strongly interact with solutes that possess large dipole moments, i.e. polar samples. Acetonitrile, dimethylsulfoxide, and dimenthylformamide are aprotic solvents and act neither as a hydrogen donor nor as a hydrogen acceptor. Aprotic solvents dissolve both organic and inorganic substances,

solvating the cation more strongly, leaving the anion relatively unencumbered and highly reactive.

A method of systematically predicting solvent strength and solvent selectivity is the Hildebrand approach (2). Solvent strength is measured by the parameter δ, which is a measure of the solvent polarity. Solvent selectivity is controlled by δ_d, δ_o, δ_a, and δ_h, which relate directly to a solvent's ability to interact with sample molecules via dispersion forces, dipole interaction, hydrogen bonding as a hydrogen acceptor, and hydrogen bonding as a hydrogen donor respectively.

Rohrschneider (2) classified solvents on the basis of their polarity and selectivity using parameters that roughly compare to those used in the Hildebrand method. The classification of these solvents is shown in Figure 12. The solvents are classified into eight groups according to their ability to interact with hydrogen donor solutes, hydrogen acceptor solutes, and polar solutes.

According to Figure 12, solvents in groups I and II strongly interact with hydrogen donor solutes, solvents in groups VII and VIII strongly interact with hydrogen acceptor solutes, and solvents in group V strongly interact with polar solutes. Therefore, an ideal combination would be three solvents, one from either group I or II, and one from either group VII or VIII, and one from group V, that would be completely miscible in each other and would form a ternary azeotrope at a given composition. One such combination was found; ethanol from group I, water from group VIII, and methylethyl ketone from group V.

These three solvents are completely miscible in each other and with a composition of 75 percent methylethyl ketone (MEK), 14 percent ethanol (ETOH), and 11 percent water (H_2O), these solvents become a

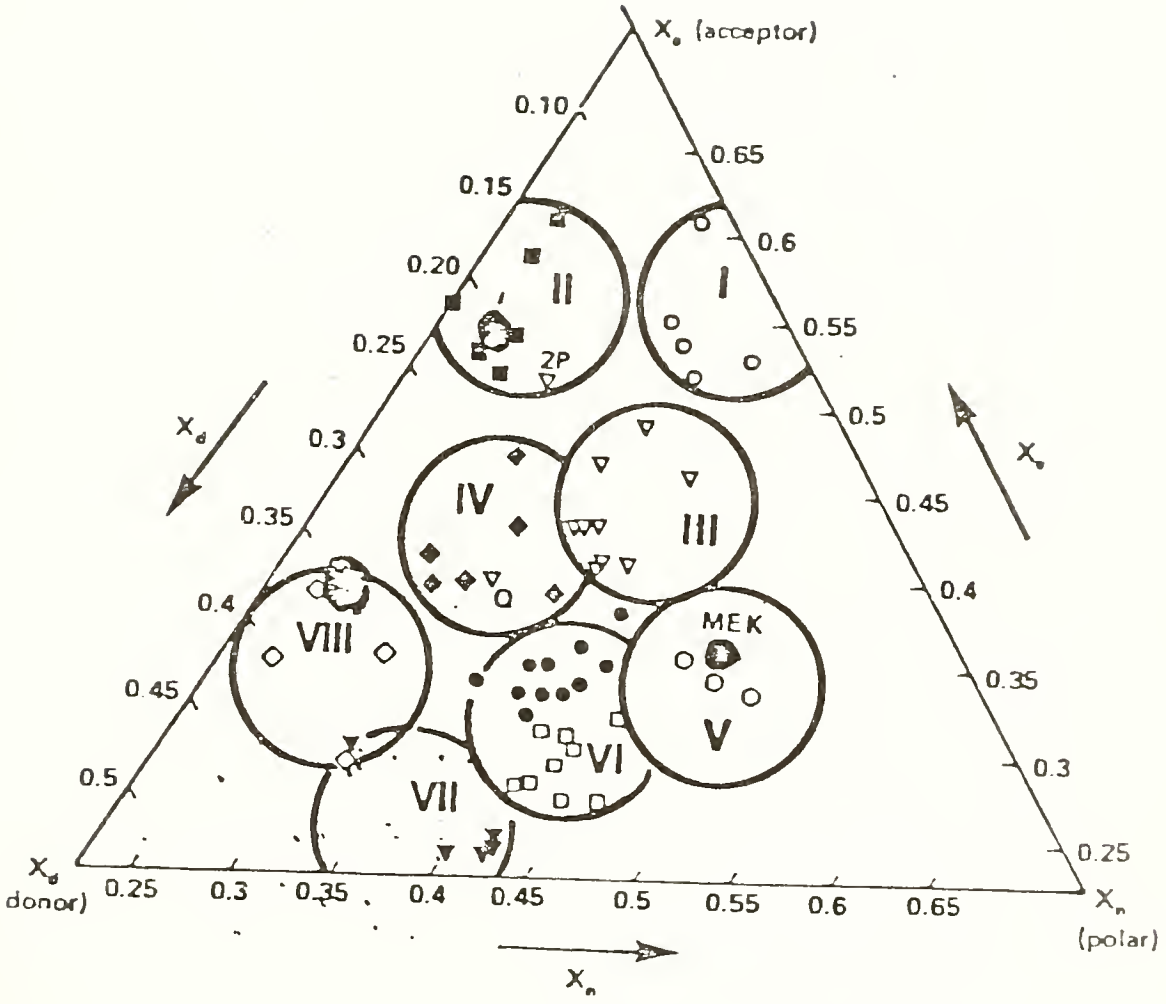


Figure 12 - Solvent Selectivity Classes

ternary azeotrope with a boiling point at 73.2°C. This was the solvent combination and composition chosen for the extraction of the organic material from the concretes or hardened cement paste samples.

Extractions were carried out for 12h, 24h, and 48h on several hardened standard cement pastes. It was determined that there were no differences between the ultraviolet absorption spectrum nor the refractive index spectrum. Peak heights and sample "fingerprints" were nearly identical for all three times of extraction. Therefore, a 12h extraction time was used exclusively in this study for extraction of the organic material from the hardened standard cement pastes and concrete samples.

Chromatographic Methods

An analytical procedure was developed, whereby the organic material extracted from a hardened cement paste or concrete was characterized using high pressure liquid chromatography.

Certain guidelines had to be considered before choosing a mode of separation. Evaluation of the separation problem was the first step, which involved determining whether the organic constituents in the sample would best be separated by molecular size or by differences in their chemical nature. So it was necessary to know as much as possible about the chemical and physical natures of the sample materials before selecting a system for chromatographic analysis. Such aspects as chemical structure, infrared absorption spectra, and solubility in various solvents were determined, owing to the fact that little specific chemical information was available from the manufacturers.

Infrared absorption spectra were obtained for each sample in the dry state, using a Beckman IR-10. The spectra, from 2000 to 600 CM^{-1}

are given in Appendix A. The infra-red patterns usually show the comparatively few and broad peaks that are characteristic of these complex mixtures of high-molecular weight materials. Their usefulness as characterizations of these materials is limited.

Owing to the small amount of information available concerning the chemical natures of the samples, size separation, i.e. gel-permeation chromatography, was not chosen as a mode of separation. In order for this mode of separation to be effective, the molecules should differ in size or molecular weight by an order of magnitude, and those of concern here do not.

The other criterion for separation, by differences in a sample chemical nature, is encompassed by the other three modes of chromatographic separation: liquid-solid chromatography, ion-exchange chromatography, and liquid-liquid chromatography.

Liquid-solid adsorption chromatography is usually best suited for separation of compounds by virtue of differences in their functional groups. This mode of separation involves use of a polar packing, e.g. Micro-porasil, a 10 micron porous silica gel, in conjunction with a non-polar mobile phase, e.g. chloroform. This method appeared initially attractive, owing to the fact that the organic materials could possibly be extracted from hardened cement paste or concrete by chloroform and

evaporation of the extraction solvent, and then resolvation with the same mobile phase. However, initial results indicated that the organic material extracted from the cement paste, either by chloroform or any other solvent or solvent combination, was not being resolved by the polar column packing. Sometimes the organic material was not retained at all, and other times the sample appeared to deactivate the column, since the column is highly susceptible to contamination by highly polar constituents.

Organic admixtures, which are usually salts of hydroxycarboxylic acids, salts of resin acids (e.g. abietic), salts of lignosulfonic acids, and salts of naphthalene or melamine sulfonic acid-formaldehyde condensation polymers, are fairly polar compounds.

It was considered that ion-exchange chromatography might be a more effective method of separation than the liquid-solid adsorption chromatography method. As discussed previously, however, there are inherent problems with this technique. For example, the available materials for ion-exchange column packings have particle sizes ranging from 30-40 microns, with a capacity factor of only 10 micro-equivalents per gram, which allows the resin to be highly susceptible to poisoning. This technique is also sensitive to changes in buffer strength, pH, and the amount of organic solvent in the mobile phase. Nevertheless, a strong-base anion exchange resin was dry packed with a 30 micron packing, and organic materials extracted from the hardened cement pastes were analyzed using different water-organic mobile phase compositions. Organic solvents used with water eluents were either methanol or acetonitrile. The results indicated little or no retention and poor resolution.

Therefore, assuming that the problem rested with the packing material and not the ionic character of the samples, three other methods which are variations of the ion-exchange method, were attempted.

These variants use differences in ionic character of the samples as criteria for separation, but use a bonded phase micro non-polar packing. These variations are called ion-suppression chromatography, paired-ion chromatography, and "soap" chromatography.

In ion-suppression chromatography, weakly ionic compounds are separated by buffering the mobile phase and thus driving the equilibrium to the nonionic state. This system was used with different samples extracted from hardened cement pastes, a non polar micro LiChrosorb RP-18 column, i.e. an eighteen carbon chain chemically bonded to a silica particle, and mobile phases of methanol-water and acetonitrile-water of different compositions. Potassium di-hydrogen phosphate was used to buffer the mobile phase in order to maintain a pH range of 2-8. If these samples are weakly ionic, then they should be in the unionized state in this pH range.

If the extracted samples are not weakly ionic, but are strongly ionic, then the sample's constituents will be ionized in the pH range 2-8 and not retained by the non-polar packing. In this case an appropriate amount of counter-ion, e.g. tetrabutylammonium hydroxide (TBAH), in a phosphate buffer, could be added, with the anion forming a large non-polar species that would be retained by the column packing.

Since the relative amounts of ionic intensity of these sample extracts were unknown, a system utilizing this method of separation was also examined. In this procedure 0.005M tetrabutylammonium phosphate was added to a liter of mobile phase, methanol-water and acetonitrite-

water at various compositions, producing a pH of 7.5. At this pH any strongly acidic compound would be totally ionized. The same non polar bonded phase column used in the ion-suppression method was used in this ion-pair approach.

Soap chromatography, the third variation, is identical to ion-pairing except for the type of counter-ion used. The counter-ion used in this technique was a cationic detergent, cetyltrimethylammonium bromide (CTAB), which is supposed to form a more stable ion-pair than the TBAH. Therefore this compound, CTAB, was also used as the counter-ion, for extracted samples, using the same procedure and operating conditions as described for ion-pair chromatography.

Valuable results were obtained by these methods. Suitable retention was obtained using the non-polar, micro LiChrosorb RP-18 column. Maximum resolution was obtained using an acetonitrile-water mobile phase at a composition of 80 percent acetonitrile and 20 percent water. Acetonitrile as described previously, is an aprotic solvent that solvates the cation, leaving the anion unencumbered and more reactive. This apparently had more importance on samples used with the ion-pairing or soap chromatography method.

The chromatogram "fingerprints" for samples extracted from hardened cement pastes were good from a resolution point of view in all three of the methods, i.e. ion-suppression, ion-pair, and soap chromatography. Problems occurred when differences between similar samples were not easily defined. Since the mobile phase, 80 percent acetonitrile and 20 percent water, in conjunction with the micro, non-polar bonded phase LiChrosorb RP-18 column packing was successful in separating the extracted

organic material by the three methods previously described, it was considered likely that this mobile phase and non-polar packing, without ion suppressants, counter-ions or buffers, would also result in good chromatographic patterns.

The use of a polar mobile phase and a non polar bonded phase packing is called reverse phase partition chromatography. Chromatographic data resulting from this method clearly indicates that the organic material extracted from the hardened cement pastes provided a unique "fingerprint" that was representative of each admixture and admixture combination. Therefore, this method was finally decided upon as that to use for the separation of all the extracted admixtures, and it did indeed perform well.

Chromatographic Identification of Organic Material Extracted from Hardened Cement Pastes

These patterns represent the results of an extraction of the organic materials from hardened portland cement pastes, followed by evaporation and resolvation in the mobile phase, and then a reverse-phase HPLC chromatographic separation.

The patterns also represent several repetitions, which showed the results to be highly reproducible for given chromatographic operating conditions. That is, the same chromatographic separation could be obtained by using a mobile phase of 80 percent acetonitrile and 20 percent water, a 10 micron LiChrosorb C_{18} column packing, a flow rate of 1.1 ml per minute, and a dual detection system similar to the type described in the "Equipment" section.

Greater differences usually occur from substance to substance in the trace produced by the ultraviolet absorbance detector than in that given by the refractive index detector. Therefore, the ultraviolet detector was used, in general, to qualitatively "fingerprint" the organic material extracted from the hardened cement pastes. On the other hand, the trace obtained from the differential refractometer usually revealed a simpler pattern, with one major peak compared to the several major peaks obtained from the more sensitive ultraviolet absorbance detector. Therefore, the major peak obtained from the RI detector was used for a semi-quantitative evaluation of the organic material extracted.

The peaks in the following patterns will be identified by number, i.e. first, second, etc., reading from left to right for both UV and RI traces. They will also be characterized by retention time in seconds,

24 s per cm (major division) of recorder paper and by intensity, according to the relative scale below:

Relative Intensity	Percent of Full Scale
Very Strong	> 80%
Strong	60-80%
Medium	30-60%
Weak	10-30%
Very Weak	< 10%

All retention times are accurate to ± ½ unit or ± 2s.

Figures 13, 14, and 15 represent admixtures A, D, and K, respectively. These admixtures are all air-entraining agents, and meet all the specifications for admixtures of this class, ASTM C 260.

In Figure 13, admixture A, which is a neutralized vinsol resin derivative, is shown a UV trace of 2 sharp peaks, the first is a medium peak at 132s and the second, a strong peak at 144s. The third, a medium peak at 178s is fairly broad with a shoulder at 184s, and the fourth, a very weak peak, is at 248s. The corresponding RI trace shows a first weak peak at 132s, which corresponds to the first peak in the UV trace. A very strong second peak is at 152s, with a shoulder at 144s, the shoulder corresponds to the second peak in the UV trace. The third peak in the RI trace is a very weak doublet at 180s and 190s, and the fourth is a weak peak at 208s. The very strong peak at 152s, the very weak doublet at 180-190s, and the weak singlet at 208s, do not have corresponding peaks in the UV trace. Peaks that are present in the RI trace that have no corresponding peaks in the UV result from the inability of the eluted

constituent to absorb radiation at or near 254 nm. Peaks that are present in the UV trace and have no corresponding peaks in the R.I., are either present in concentration below the detectable limit of the differential refractometer at a given operating sensitivity or have by unusual chance the same refractive index as the mobile phase in the reference cell.

In Figure 15, admixture K, which is also a neutralized vinsol resin derivative from a different producer shows a UV trace with two sharp peaks. One is a very strong peak at 134s, and the second is a very strong peak at 146s. The third peak is weak at 178s, and there is a very weak peak at 252s. The RI trace shows a medium peak at 136s, which probably corresponds to the first peak in the UV trace. A second strong peak at 152s, a very weak peak at 184s, and a weak peak at 194s make up the rest of the RI trace. Figure 14, for admixture D, which is a triethanolamine salt of a sulfonated hydrocarbon, shows a UV trace with a strong first peak at 132s with a shoulder at 130s. A second peak, medium at 142s, and a third peak, a medium doublet at 172s and 180s complete the UV trace. The RI trace shows a very weak doublet at 132s which probably corresponds to the first peak in the UV trace. A second peak, medium at 148s and a very weak peak at 186s complete the RI trace.

This detailed account of the chromatographic results for the air-entraining agents shows that these admixtures can be positively identified by a "fingerprint" chromatogram that is unique.

Air-entraining agents A and K are derived from the same basic substance, vinsol resin. Their chromatograms are similar in general, yet they differ in small detail. The first three peaks of the UV trace

in Figure 13 for admixture A compare closely with those of admixture K in Figure 15, within an experimental error of about 2s. The position of the strongest peak in the RI trace is also the same at 152s. Yet there are differences in the third peak of the UV trace. Admixture A has a retention time of 178s for its third peak in the UV trace but this peak is broad and has a shoulder at 184s. The third peak in the UV trace for admixture K, at 178s is not so broad and has no shoulder associated with it. There is also a major difference in the intensities of the third peaks, relative to those of their first and second peaks. These small differences show how two admixtures can be uniquely identified even though they are derived from the same parent substance.

Admixture D, which also is an air-entraining agent, is derived from a different chemical compound than admixtures A or K. The UV trace in Figure 14 is obviously different than those of Figure 13 or 15. The position of the major peak is the RI trace of admixture D, at 148s, is also different than the major peak of the RI traces of admixtures A or K. Further examination of Figure 14 shows that the RI trace for admixture D has fewer peaks than the RI traces of admixture A or K. Also, the UV trace of admixture D is slightly more complex and distinctive than the UV traces of admixtures A and K.

The following discussion represents a general description of the chromatographic patterns of single admixtures, which conform to the requirements of ASTM C-494. The descriptions are based on the retention time values as well as on relative intensities of the peaks. It should be noted that changes in solvent composition, i.e. viscosity of the mobile phase, column length, packing particle size, and flow rate can all contribute to different values of retention times and relative intensities

and so can change the patterns obtained. For this reason, these patterns cannot be considered invariant, in the sense of absorption spectra, x-ray diffraction patterns, and the like.

Figures 16, 17, 18, and 19 represent samples B, L, E, and F, respectively. These are all water-reducing admixtures, type A, of C 494. Admixtures B and L, according to the information provided by their producers, are based on multicomponent polymeric compounds. Examination of Figures 16 and 17 shows obvious differences in the chromatograms, both for the UV and RI traces. In Figure 16, the first two peaks at a 3:2 ratio are followed by a rather broad trailing peak that may contain a shoulder. The RI trace basically consists of a strong peak at 152s. Figure 17, the first peak in the UV trace is a sharp singlet followed by a shoulder and a weak peak. Then follows a quartet with an approximate height ratio of 1:2:2:1.

Figures 18 and 19 represent two water-reducers that come from the same producer. Admixture E is supposedly a salt of a lignosulfonic acid with triethanolanine added. Admixture F is supposedly similar to E, except another saccharide ingredient was added. The UV traces for both appear similar. Retention times for the first three peaks for admixture E are 133s, 144s, and 174s. The retention times for the first three peaks for admixture F are 135s, 150s, and 174s. The RI traces are also similar except for the size of the last peak. It appears that the position of the second peak in the UV trace is the deciding factor differentiating these two admixtures. The major peak in the RI for admixture E, Figure 18, does not have a corresponding peak in the UV trace. But, the major peak in the RI trace of admixture F, Figure 19, does have a corresponding peak in the UV, the second peak at 150s.

Figure 20 represents sample M, which is the only type B, retarding admixture investigated. The majority of retarding admixtures are also water reducers, i.e. type D of C 494. Admixture M, in Figure 20, is quite complex with respect to both the UV trace and the RI trace. The first peak in the UV trace is fairly sharp with a triad of peaks following, with retention times of 160s, 182s, and 210s. The RI trace shows two very strong peaks, one at 154s and another at 212s. The very strong peak at 154s has a corresponding peak in the UV, a small shoulder at 154s, and the corresponding UV peak for the other very strong peak, at 212s, is probably the UV peak at 210s.

Figures 21 and 22 represent samples J and N, which are set-accelerating admixtures, type C of C 494. Admixtures J and N are basically calcium formate, and a multi-component product primarily calcium chloride, respectively. Admixture J has three major peaks in the UV trace at 142s, 148s, and 154s. The RI trace has a positive peak at 146s and a negative peak at 158s at a 4.5:1 height ratio. The negative peak is due to a sample whose RI is less than the refractive index of the carrier solvent. Admixture N, in Figure 22, has one sharp peak in the UV trace at 144s. The RI trace has a positive peak at 146s and a negative peak at 160s again at approximately a 4.5:1 ratio.

Figures 23, 24, 25, 26, and 27 represent samples C, O, G, H, and I respectively. These are all water-reducing and set-retarding admixtures, type D of C 494. Admixtures C and O, are metallic salts of hydroxy-carboxylic acids. In Figure 23, for admixture C, the UV trace is characterized by a very strong peak at 132s followed by two small sharp peaks and a broader peak at 156s. In Figure 24, admixture O, the UV

trace is characterized by a very strong peak at 130s, followed by two small sharp peaks and another peak at 182s. The first three peaks in the UV trace appear to be characteristic of hydroxycarboxylic acid salts, with the major difference being the position of the fourth peak in Figure 23 and the fifth peak in Figure 24. The first two peaks in the RI traces for both sample C and O are also similar, except that in Figure 24 there is a peak at 190s for which Figure 23 has none.

Samples G, H, and F, in Figures 25, 26, and 27, are type D admixtures from the same producer. Sample G is a salt of a lignosulfonic acid, sample H is a salt of a gluconic acid, and sample I is like sample G with a saccharide material added. The UV traces in Figure 25, 26, and 27 are all similar. The first major peak is sharp with a preceding shoulder, the second peak in Figure 25 is a doublet. In Figure 26, it is a singlet, and in Figure 27, there are three small peaks. The last peak in the UV trace is very strong and board at 172s in Figure 25 for admixture G. It is less than half that intensity, but again broad, in Figure 26, for admixture H. It is a medium sharp peak at 182s, in Figure 27 for admixture I. The RI traces in Figures 25 and 26, for admixtures G and H respectively, are again similar, and that of Figure 27, for admixture I, is somewhat different. Therefore, the differences between these three admixtures can be determined by the number of peaks between the first and last major peaks in the UV trace and also by the intensity of the last peak particularly for admixture G and H, since the retention time of the last peak for admixture I, Figure 27 is much later than for admixtures G and H.

Figures 28, 29, 30, and 31 represent samples P, Q, R, and S respectively, which are all super water-reducing admixtures. Admixtures

P and R are salts of naphthalene sulfonic acid- formaldehyde condensation polymers. Admixture Q is a polymer of a salt of melamine sulfonic acid partially condensed with formaldehyde. Admixture S is supposedly a combination of both types. Examination of Figures 28 and 30 shows the similarity of these admixtures, which are supposedly based on the same polymeric material, yet are from different producers. The first very strong peak in the UV trace for both admixture P and R is at 132s. The middle peak in Figure 28 shows two singlets, whereas the middle peaks in Figure 30 show a singlet, followed by a doublet, which is also followed by a single peak. The characteristic "fingerprint" of these two samples is the doublet at 344s and 370s. The doublet for admixture P is at a 1:2.5 ratio, whereas for admixture R it is at a 1:1.6 ratio. The first major peak in the RI at 152s is also the same for both admixtures, the RI trace for admixture R, Figure 30, shows another peak at 206s. Admixture Q, Figure 29, shows a completely different "fingerprint" than that of Figure 28 and 30. RI peaks at 152 and 206s are similar to those of admixture R, in Figure 30, but the UV trace is different, with peaks at 142s, 154s, and a strong doublet at 176-184s. Admixture S, Figure 31, shows an RI trace similar to both admixture R and Q. However, the UV peaks appear to be like those of admixture R at 132s, 144s, 154s, 172s, and 200s. The UV fingerprint in Figure 31 does not show the characteristic 2 peaks at 344s and 370s as does admixture P and R.

Figure 32 represents a chromatogram for triethanolamine, at a concentration of 0.05 percent by weight of the cement used to make the paste. This admixture was included because of the recent interest in its chemical determinations (26, 27, 28). The UV trace has major peaks at 148s, 168s, and 222s, and minor peaks at 162s, 190s, and 316s.

The RI trace shows two peaks at 166s and 222s.

Figure 33 represents a chromatogram of a standard cement paste sample, prepared with Type I portland cement, laboratory classification 323, and water, at a water-cement ratio of 0.4 to which no admixture was added. The UV trace shows a weak peak at 140s and a very weak peak at 202s. The RI trace shows a very weak peak at 140s and a weak peak at 168s. These peaks appear to have an insignificant effect on the qualitative "fingerprinting" of the admixture extracts as well as on the semi-quantitative determination based on the RI trace. They may be caused by the presence of grinding aids that may have been used in the manufacture of the cement.

The next figures represent the chromatograms resulting from the organic materials extracted from hardened cement paste containing a combination of admixtures, i.e. an air-entraining agent plus another admixture either a Type A, Type B, Type C, Type D or a super water-reducing admixture.

Figures 34, 35, 36, and 37 represent samples that contain an air-entraining agent and a water-reducer. Figures 34 and 35 represent two samples with a vinsol resin derivative as its air-entraining agent and a multi-component polymer compound as its water-reducing admixture. Examination of these two Figures illustrates the diagnostic value of this method of distinguishing between two samples that apparently have the same chemical compounds added to them but come from different producers. Figure 36 represents an air-entraining agent, derived from a sulfonated hydrocarbon, and a water reducer derived from a ligno-sulfonic acid with added triethanolamine, sample D-E. Figure 37

represents the same air-entraining agent with a water-reducer based on a lignosulfonic acid-triethanolamine-saccharide mixture. Examination of these figures, particularly the UV traces shows that the "fingerprint" chromatograms obtained are definitely characteristic of the samples extracted from the hardened cement paste.

Figure 38 represents a sample containing an air-entraining agent and a set-retarding admixture. Examination of this figure reveals a unique but unusual "fingerprint", which does not give a complex UV or RI trace.

Figures 39 and 40 represent samples containing an air-entraining agent and a set-accelerator. Sample D-J is a sulfonated hydrocarbon air-entraining agent and a calcium formate accelerator, while sample K-N is a vinsol resin air-entraining agent and a calcium chloride-based multicomponent product. The differences between the UV traces of both figures is distinctive, as with the accelerating admixtures alone. The RI traces also has the characteristic, strong positive peak followed by a weak negative peak, which was found for the accelerators alone.

Figures 41, 42, 43, 44, and 45 represent samples consisting of an air-entraining agent and a water-reducing and set retarding admixtures. Figures 41 and 42 represent two samples that both have a vinsol resin derivative as its air-entraining agent and a hydroxylated carboxylic acid salt as its water reducing retarder, but come from different producers. Examination of both of these figures shows unique UV chromatograms which again displays the diagnostic value of the method. Figures 43, 44, and 45 represent samples containing the same air-entraining agent, i.e. sulfonated hydrocarbon and three different

Type D admixtures - a salt of a lignosulfonic acid, a gluconic acid salt, and lignosulfonate plus saccharide. Examination of these figures shows three unique UV fingerprints, by which it would be easy to distinguish among these samples extracted from hardened cement pastes or concretes.

Figures 46, 47 and 48 represent samples containing air-entraining agents and super water-reducing admixtures. In Figure 46 the air-entraining agent is based on a vinsol resin and the super water-reducer in a polymer of naphthalene sulfonic acid partially condensed with formaldehyde. In Figure 47, the air-entraining agent is based on a sulfonated hydrocarbon and the super water-reducer is a polymer of melamine sulfonic acid partially condensed with formaldehyde. In Figure 48, the air-entraining agent and super water-reducer are based on the same chemical compounds as in Figure 46, except that both admixtures come from a different producer than those of sample K-P. Examination of Figure 46, 47, and 48 reveals the large difference in the UV and RI traces of Figure 47 as compared with Figures 46 and 48. In Figures 46 and 48, both UV and RI traces look similar, at least in the number of peaks, and peak heights. Both also have the characteritic two peaks with the large retention times of the naphthalene sulfonic acid-formaldehyde condensate samples, shown in Figure 28 and 30. The differences in the UV trace of samples K-P and A-R are in the retention times of the UV peaks. In Figure 46, the retention times for sample K-P are 136s, a doublet at 154s, 180s, 214s, 350s, and 378s, while the retention times for sample A-R, Figure 48, are 128s, a doublet at 144s, 172s, 208s, 342s, and 368s.

Figure 49 represents a test made to reveal possible chemical reaction that might take place when an admixture is added to a cement paste containing an air-entraining agent.

This figure represents the results of a combined sample in which the extracts of separate pastes were combined before measurement. One paste contained admixture K, a vinsol air-entraining agent, and the other contained admixture O, a water-reducing retarder. Each was extracted in the usual way and the two extracts were combined and evaporated to dryness, resolvated with the mobile phase, and injected into the chromatograph. Comparing Figure 49, with Figure 42, which is for a combination of these two admixtures in the same paste, shows a difference in both the UV and RI traces. It can be concluded that the extracted material from the sample K-O, in which the admixtures were added to the same paste, is different than in sample K+O, where the admixtures were extracted from separate pastes, and later combined. This difference accounts for the fact that the peaks obtained from the chromatograms of extracts from cement pastes containing a combination of admixtures, are not additive combinations of patterns of extracts from cement pastes containing the individual admixtures.

Such results emphasize the need to provide a standard sample of a cement paste containing the admixture or admixtures in question, and preferably containing the cement used in the unknown, cured for a reasonable time (at least 7 days), and subjected to any unusual conditions, such as higher temperature curing, to which the unknown sample was also subjected.

CHAPTER VII - CONCLUSIONS

The following conclusions are based on the chromatograms obtained and are restricted to the admixtures and other materials used. They do not necessarily apply to other organic admixtures, although there is no logical reason why they should not behave similarily.

1. It is concluded that organic admixtures can be extracted from hardened cementitious materials by a mixture of 75 percent methyl ethyl ketone, 14 percent ethanol, and 11 percent water, a constant boiling azeotrope, and using a Soxhlet extraction procedure.
2. The extracted materials, when dried and redissolved in a carrier phase of 80 percent acetonitrile and 20 percent water, and subjected to high pressure liquid chromatography with a micro- C_{18} column, yield ultraviolet detector traces that are unique for the substance in question and can be used, along with the results from companion standards of hardened cement paste containing the admixture, to identify the admixture present.

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VITA

APPENDICES

APPENDIX A

APPENDIX A

Figures 50 through 68 show the mid-range infra red spectra of the admixtures. They were dried and prepared in the usual KBr mounts and the spectra were recorded with a Beckman IR-10.

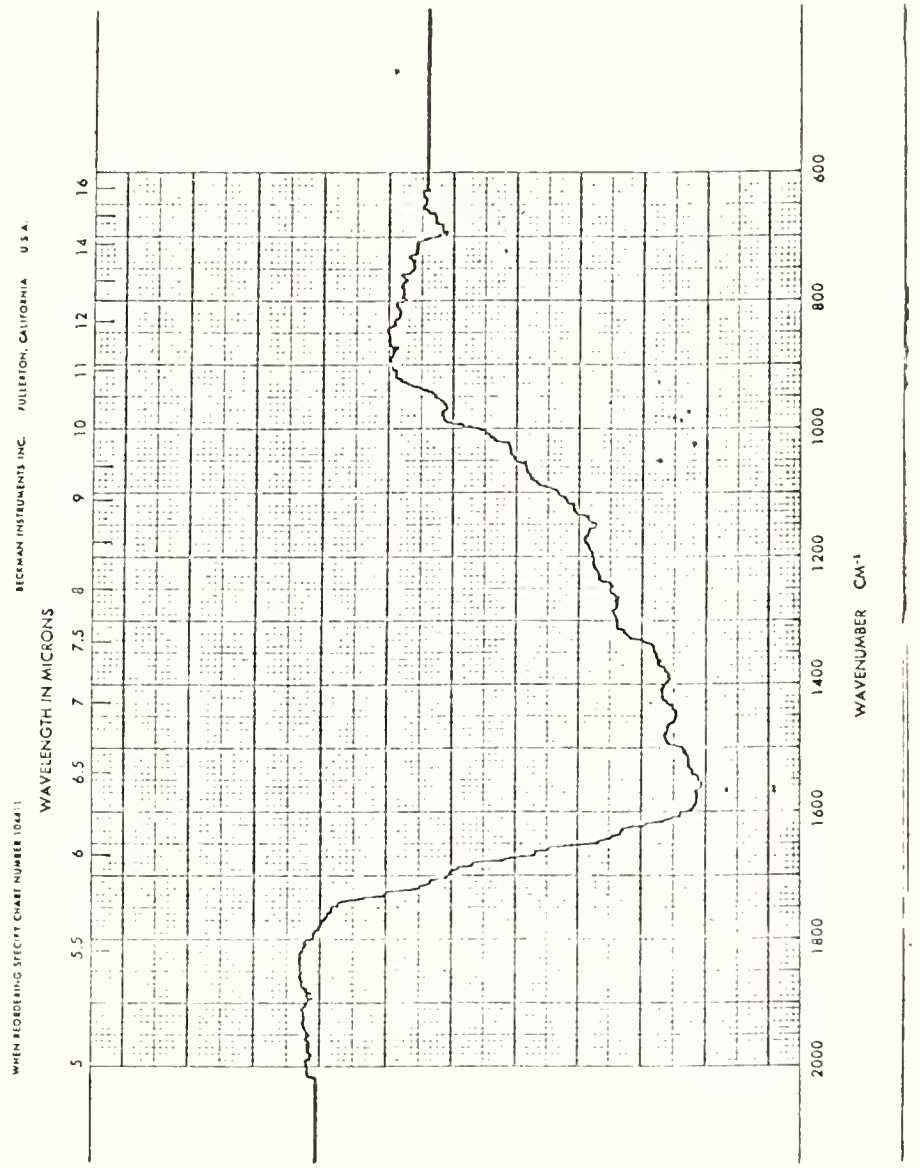

Figure 50. Infrared Spectrum - Admixture A

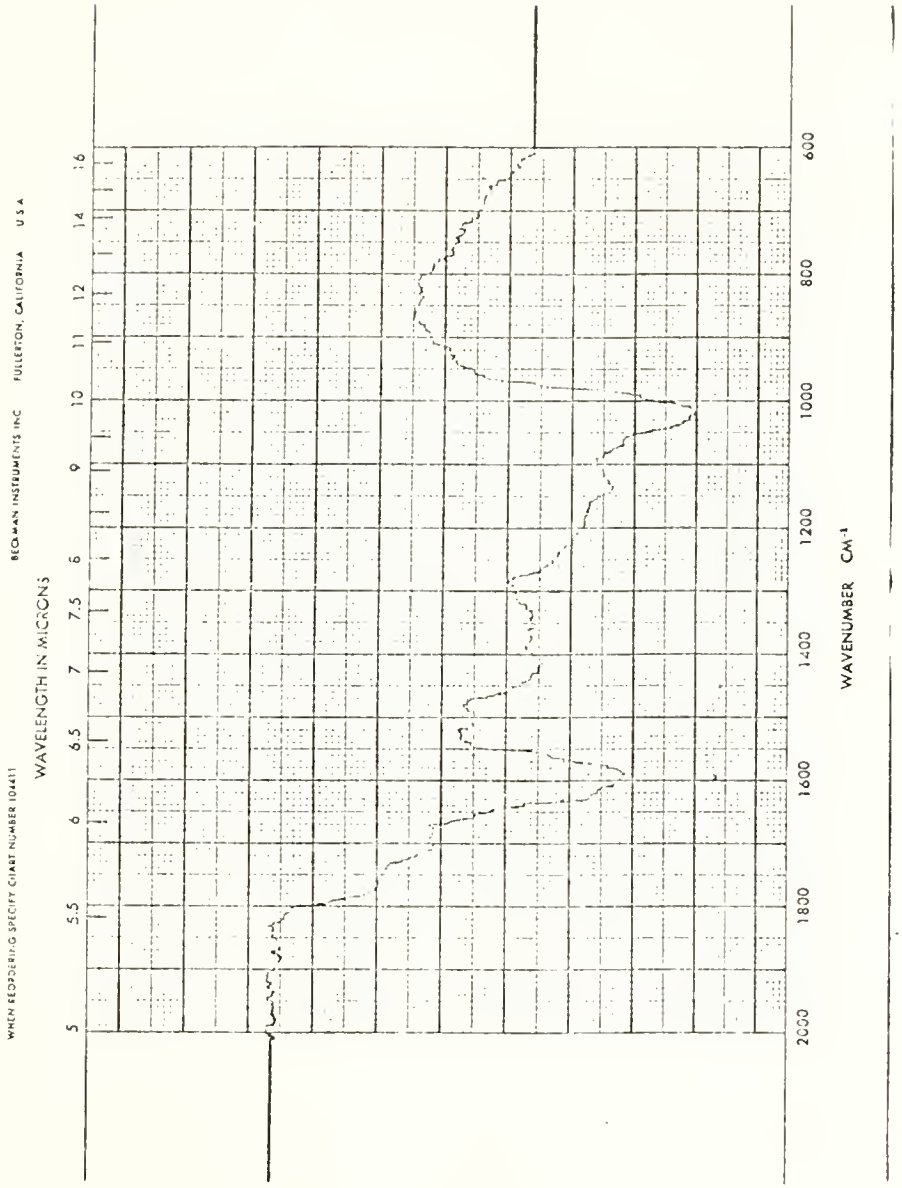

Figure 51. Infrared Spectrum - Admixture B

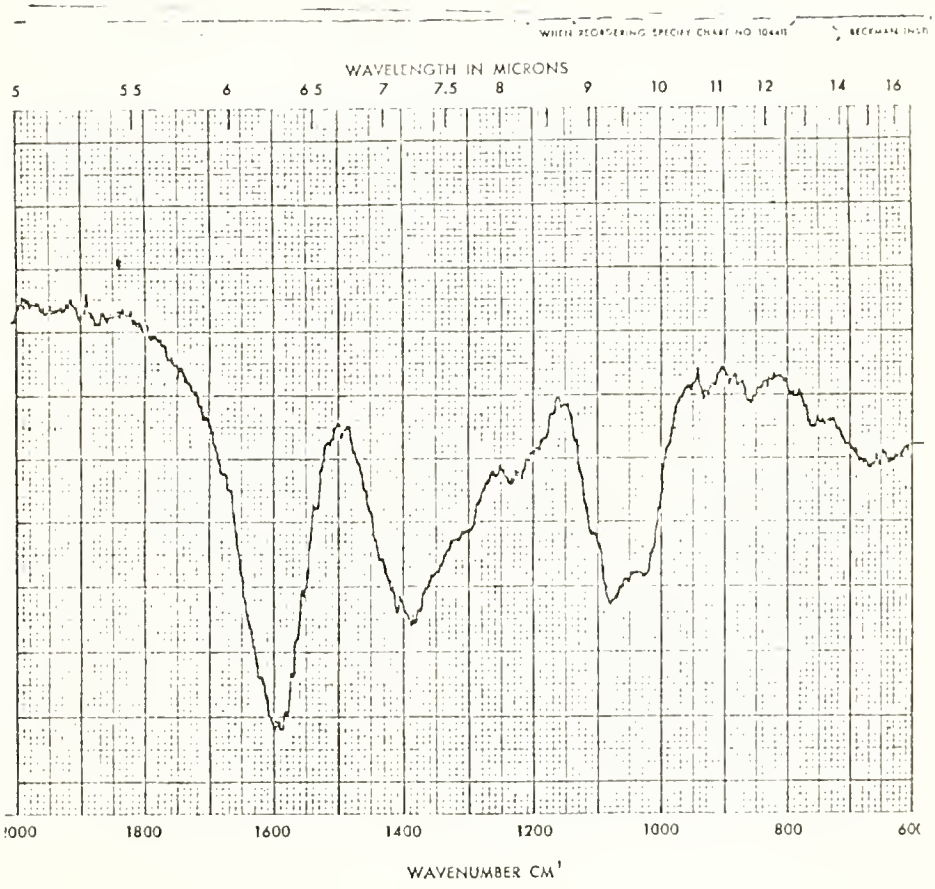

Figure 52. Infrared Spectrum - Admixture C

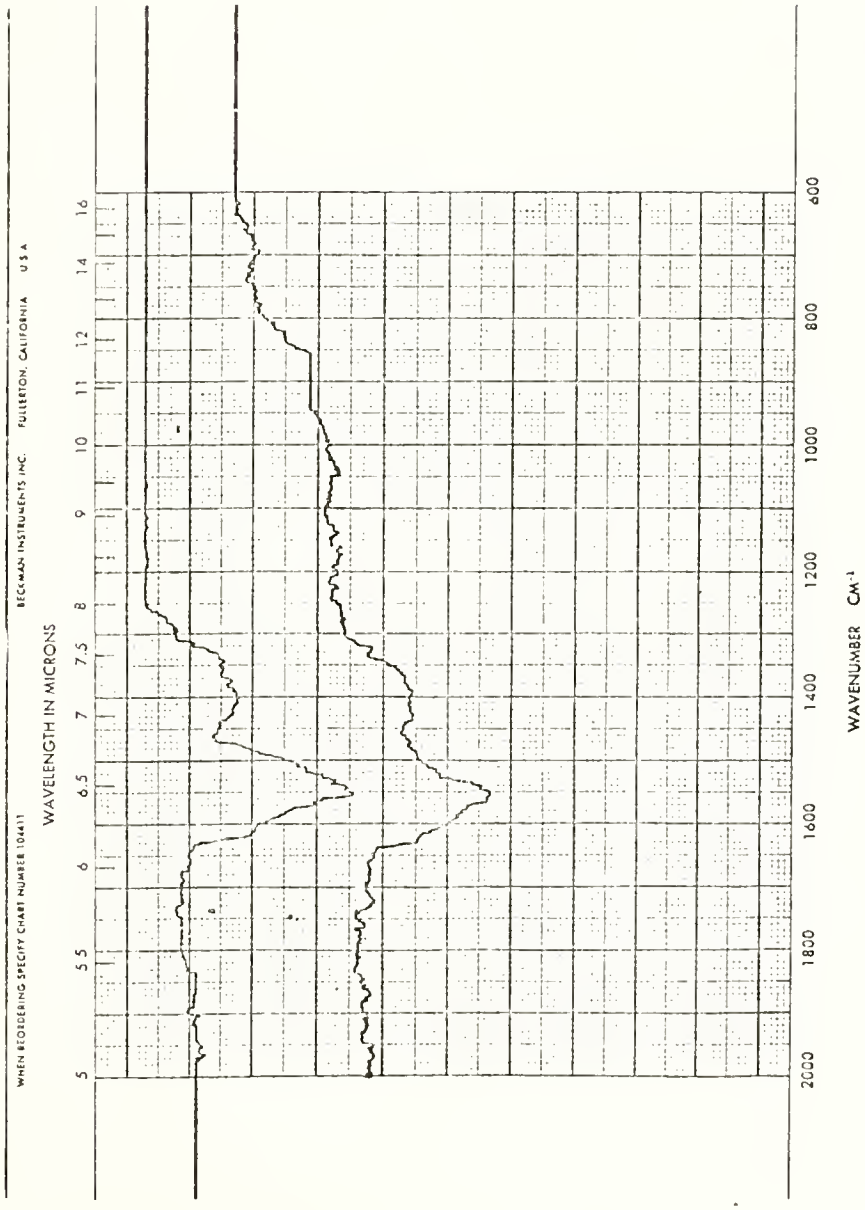

Figure 53. Infrared Spectrum - Admixture D

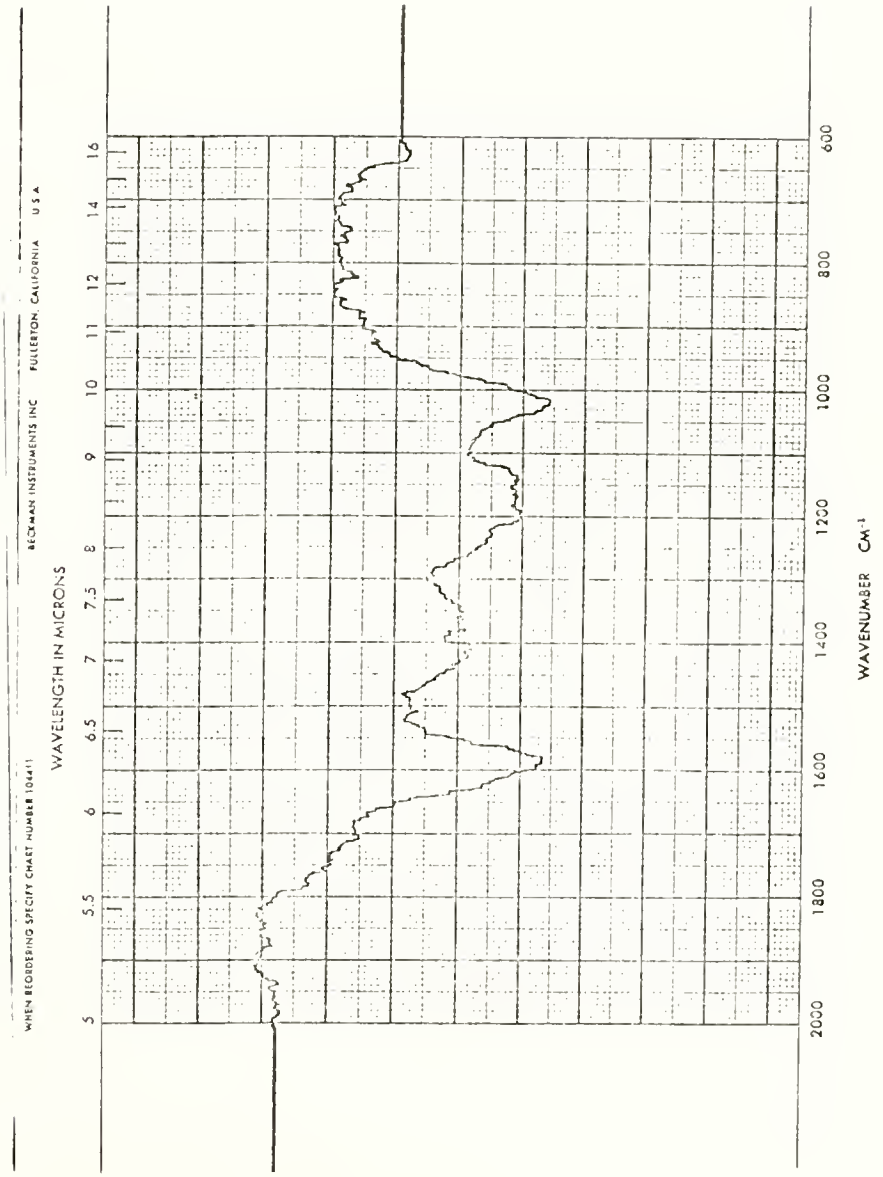

Figure 54. Infrared Spectrum - Admixture E

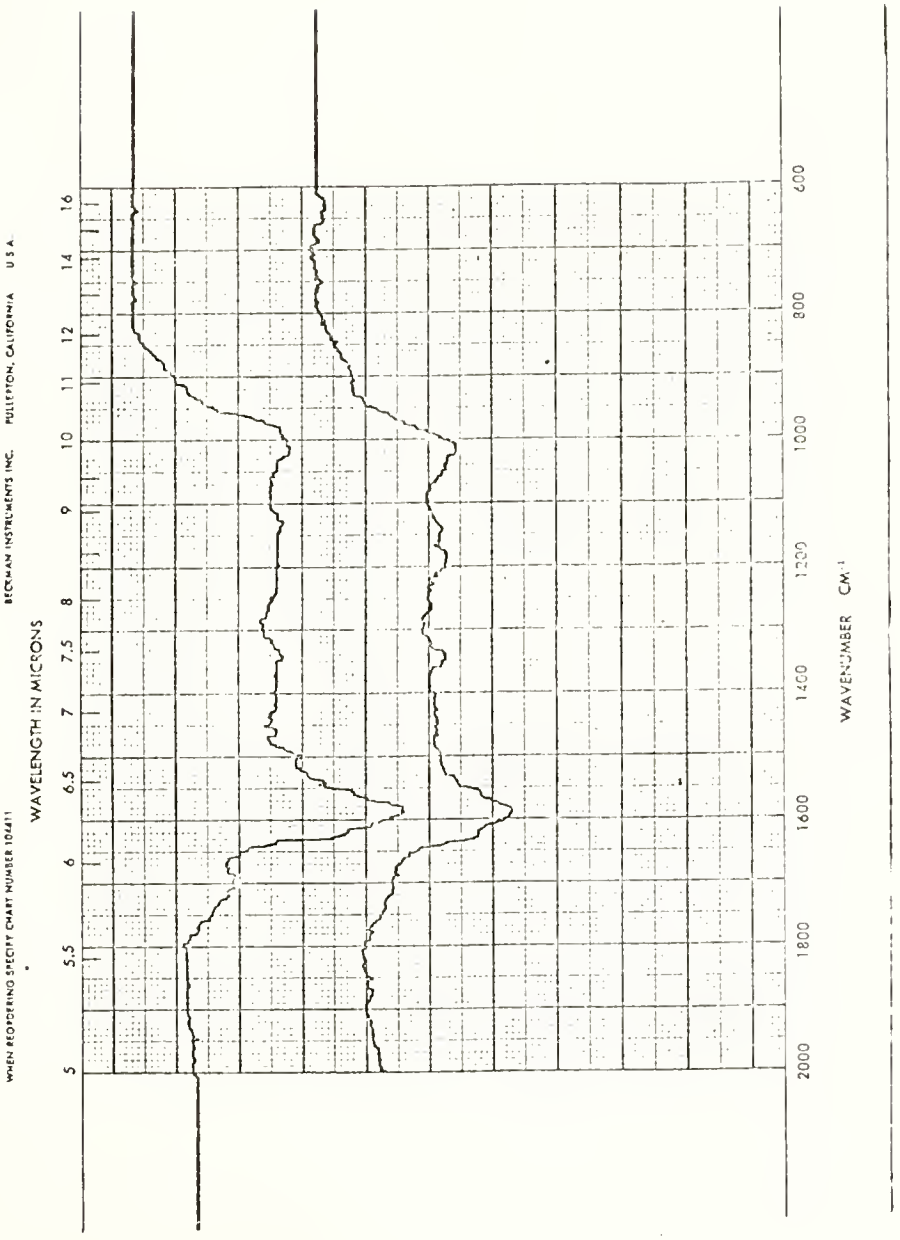

Figure 55. Infrared Spectrum - Admixture F

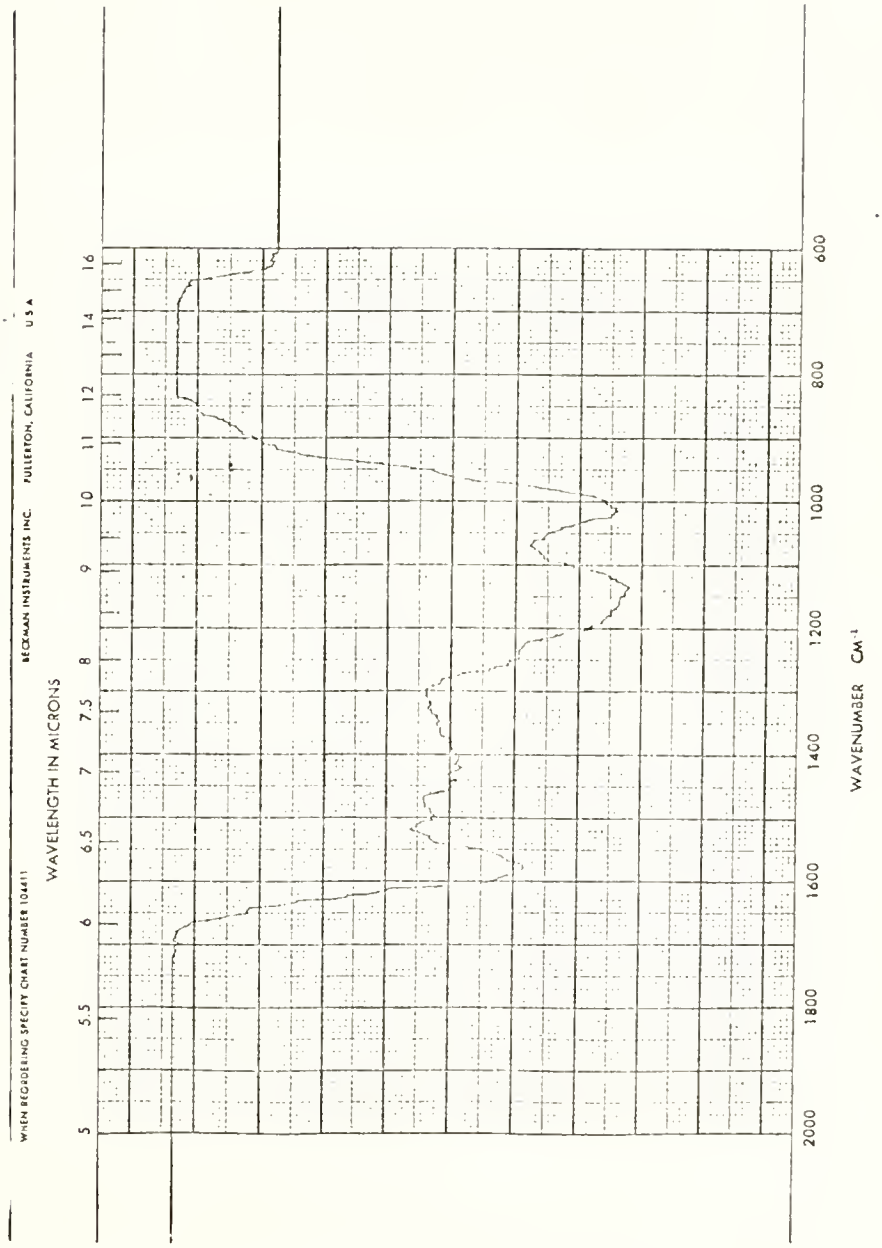

Figure 56. Infrared Spectrum - Admixture G

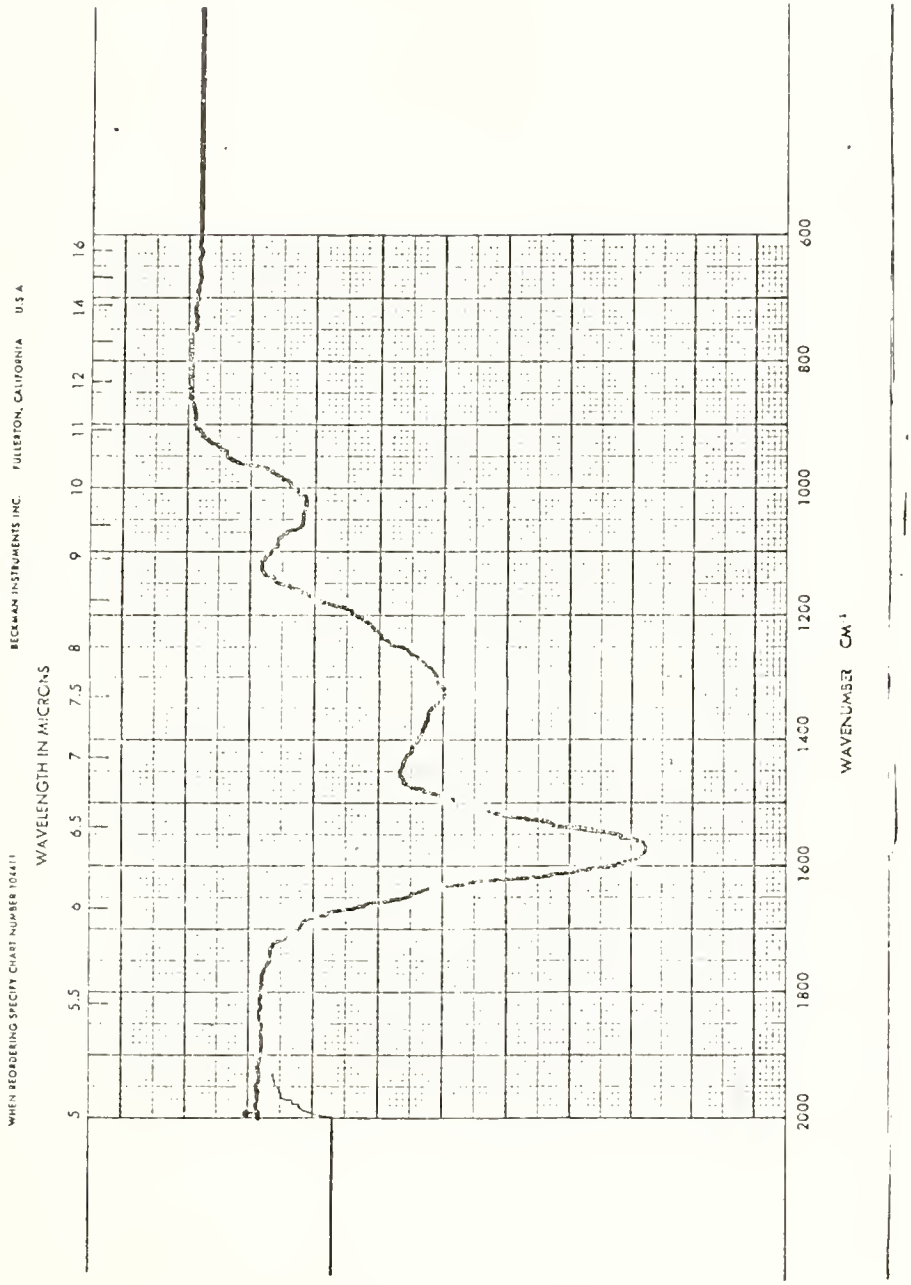

Figure 57. Infrared Spectrum - Admixture H

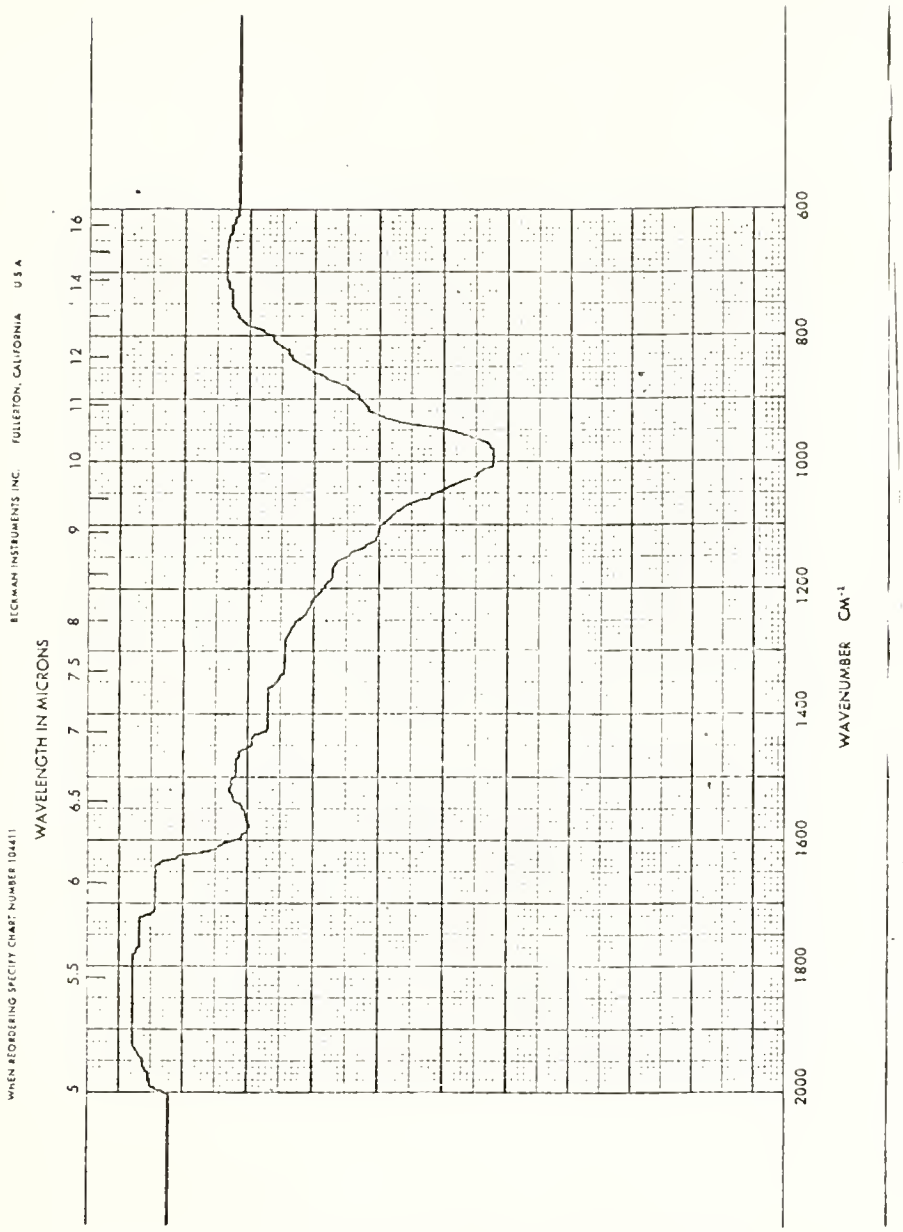

Figure 58. Infrared Spectrum - Admixture I

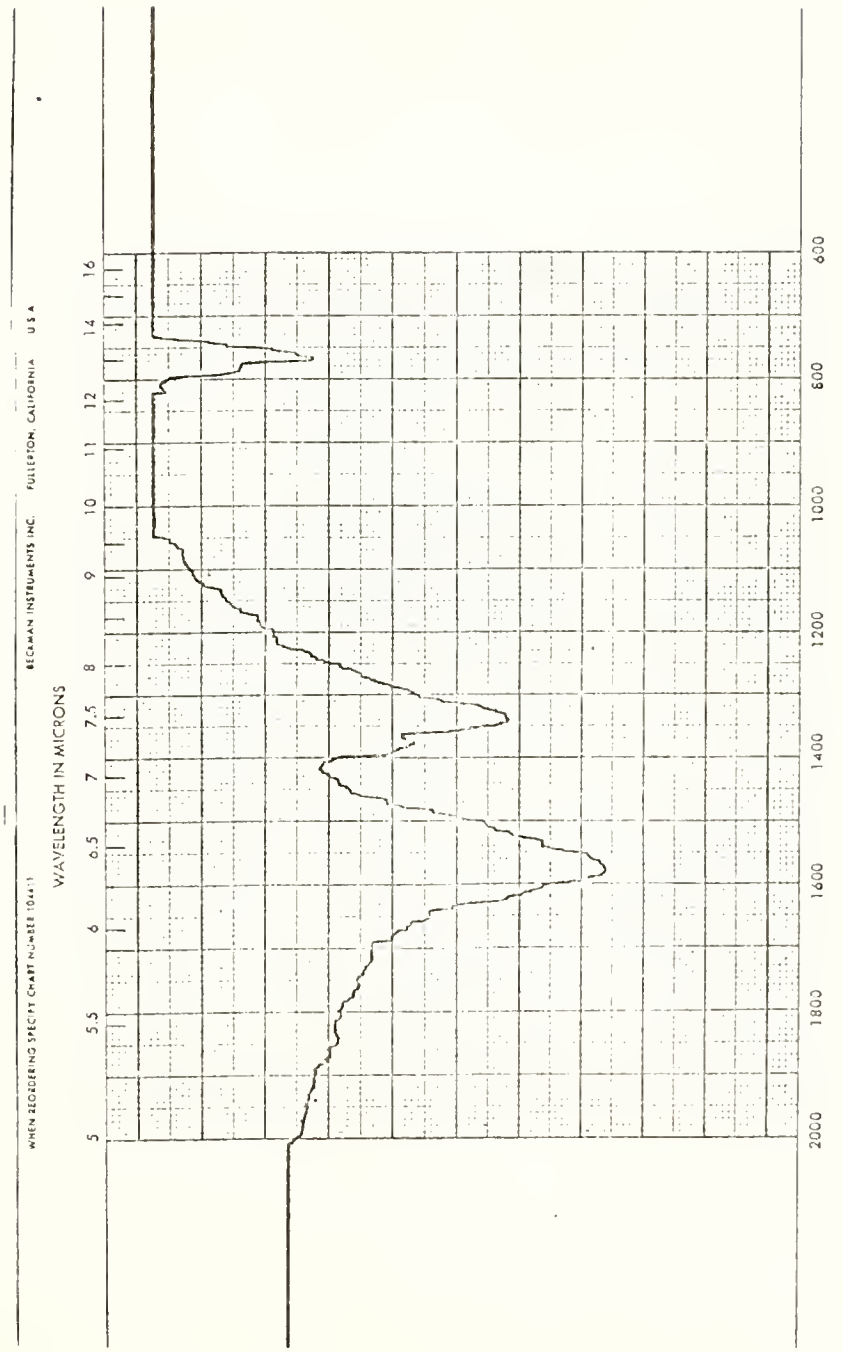

Figure 59. Infrared Spectrum - Admixture J

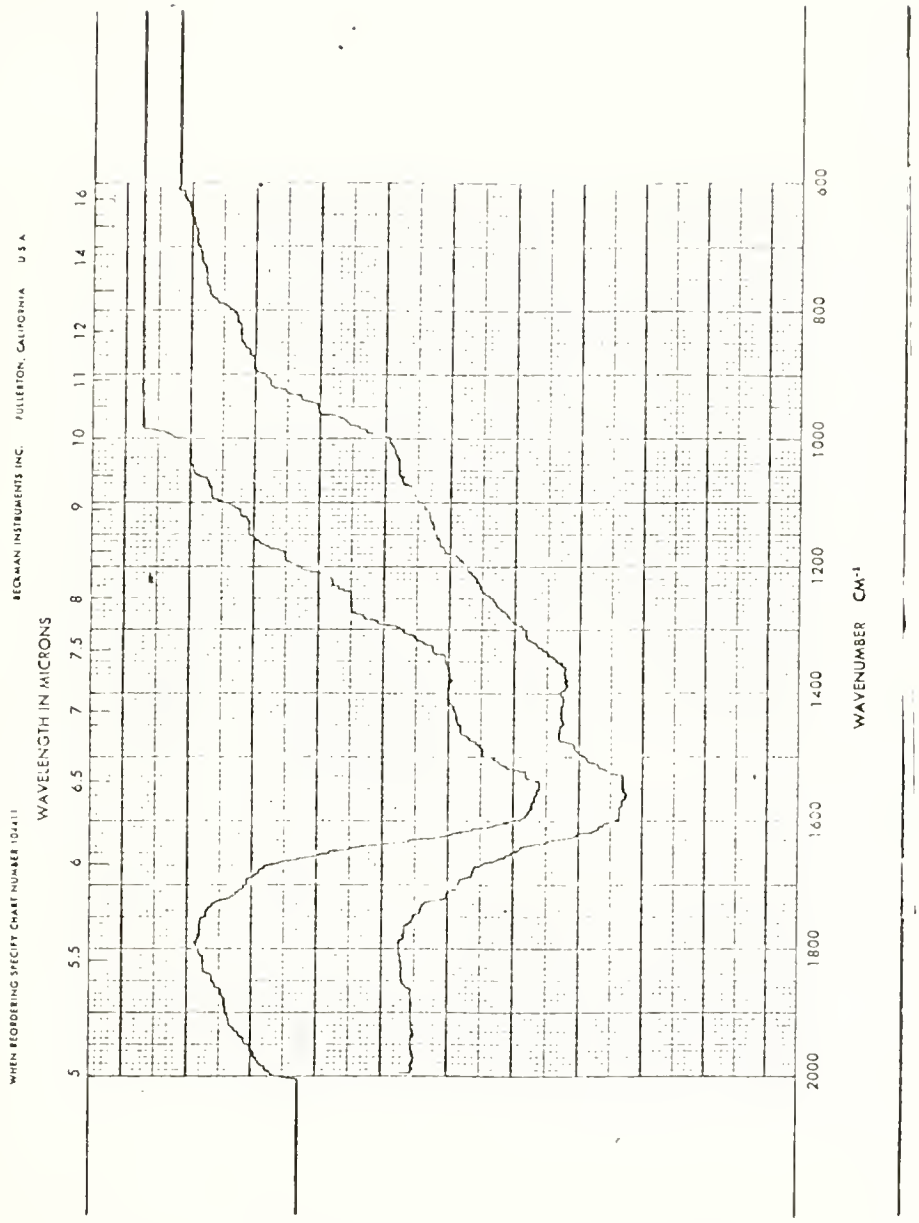

Figure 60. Infrared Spectrum - Admixture K

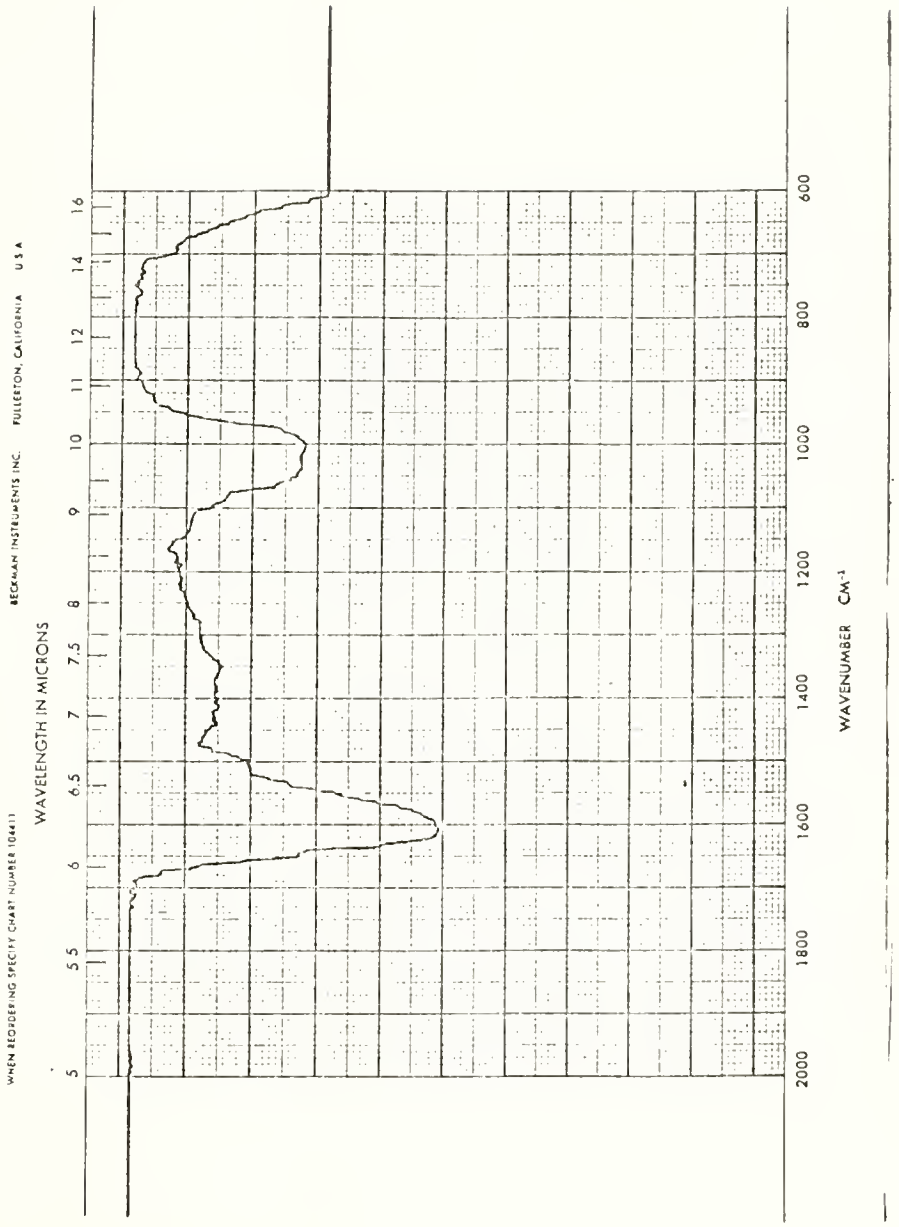

Figure 61. Infrared Spectrum - Admixture L

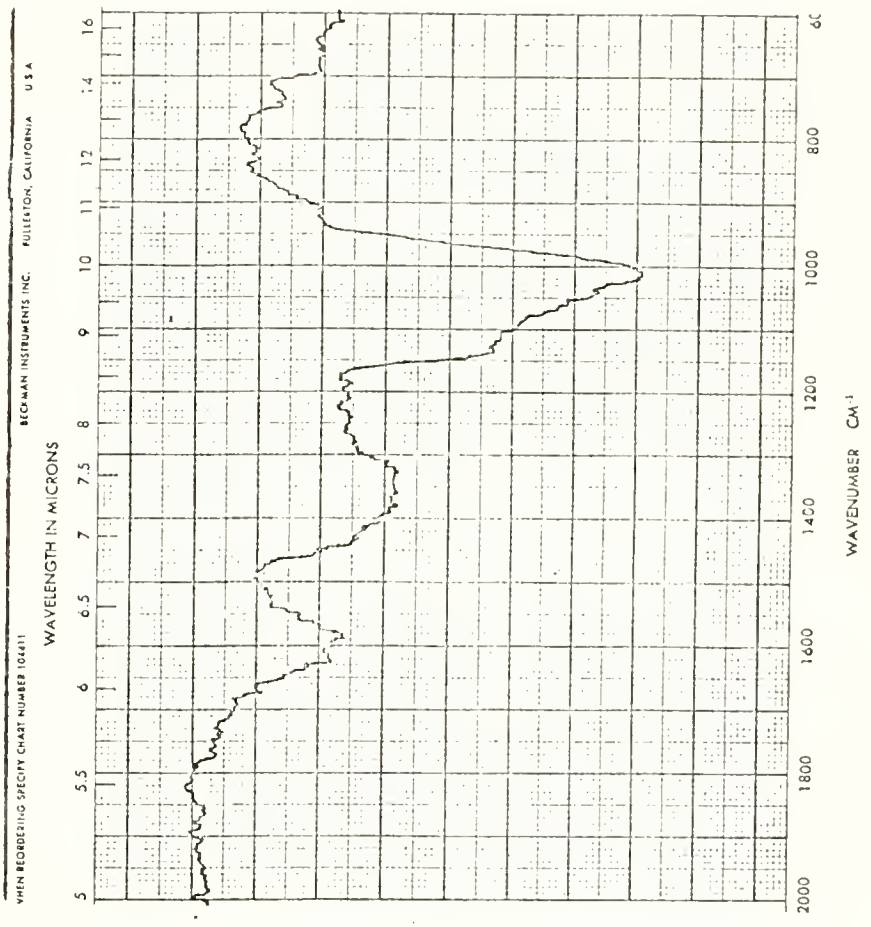

Figure 62. Infrared Spectrum - Admixture M

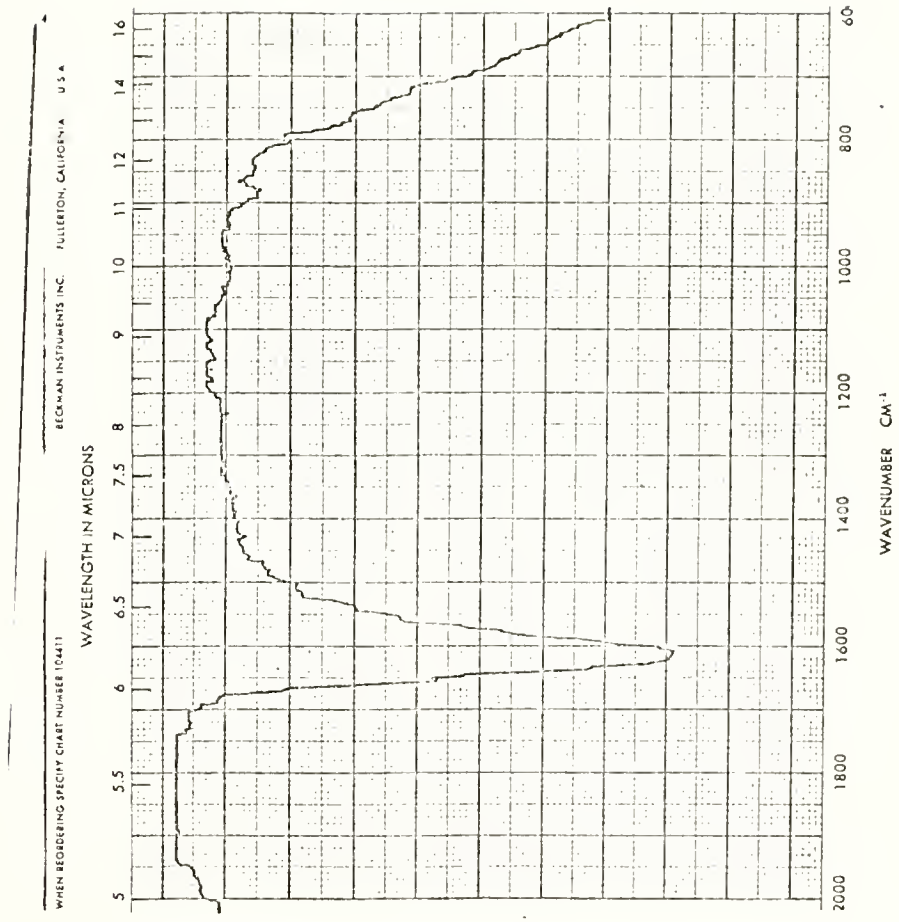

Figure 63. Infrared Spectrum - Admixture N

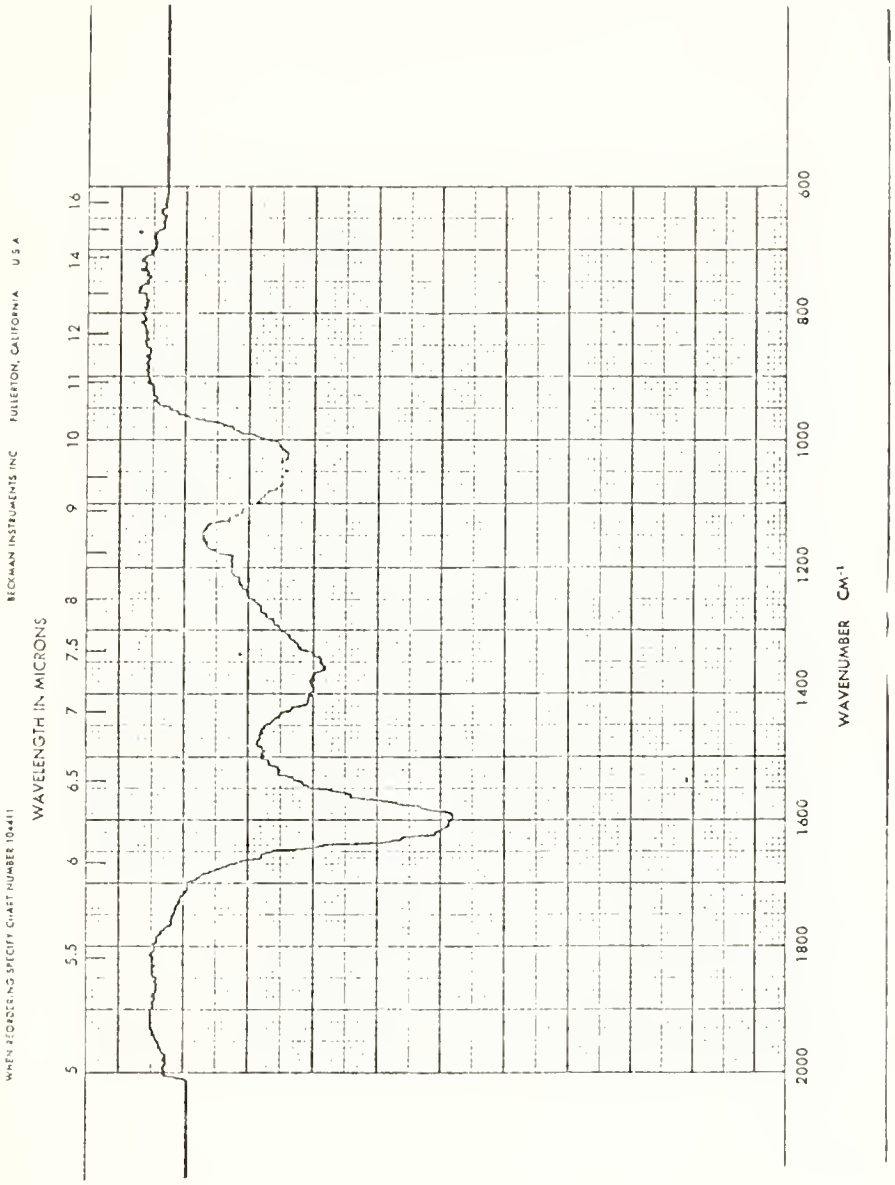

Figure 64. Infrared Spectrum - Admixture 0

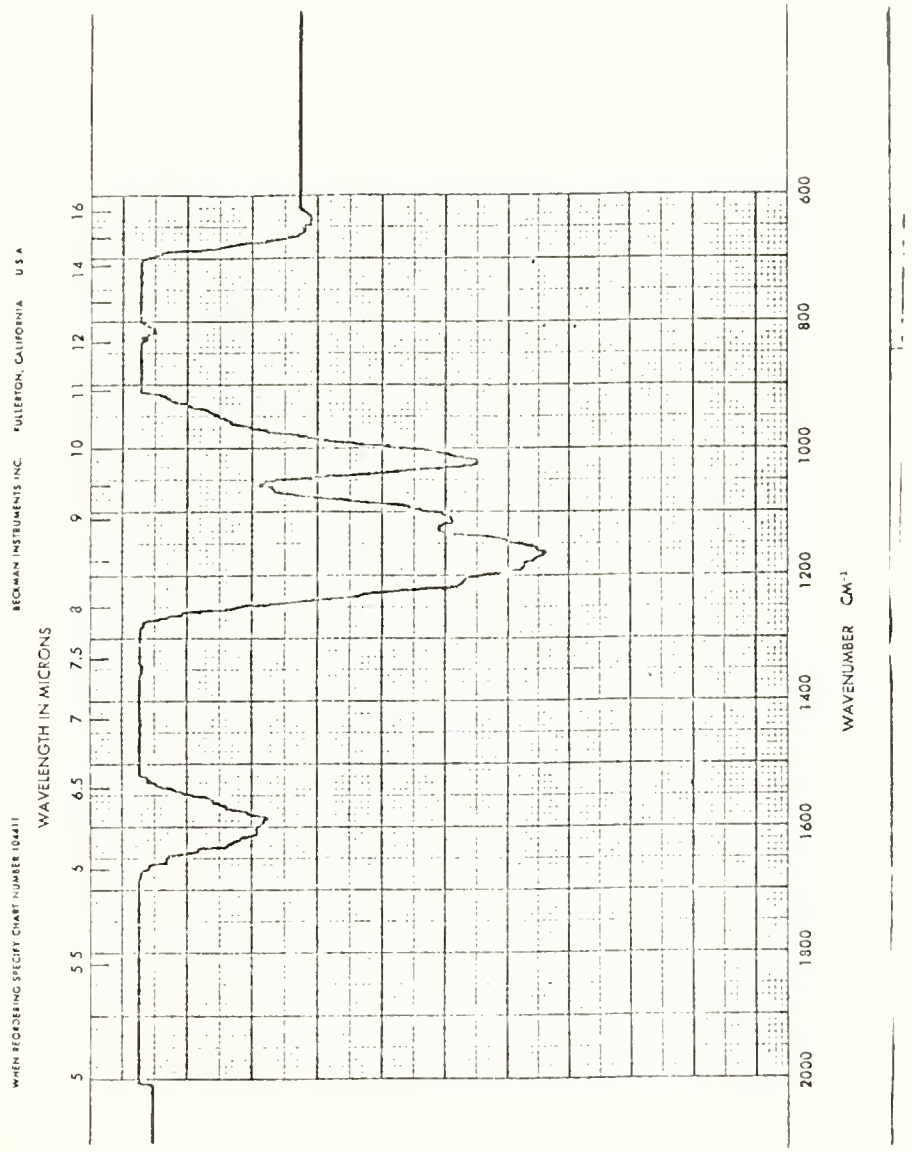

Figure 65. Infrared Spectrum - Admixture P

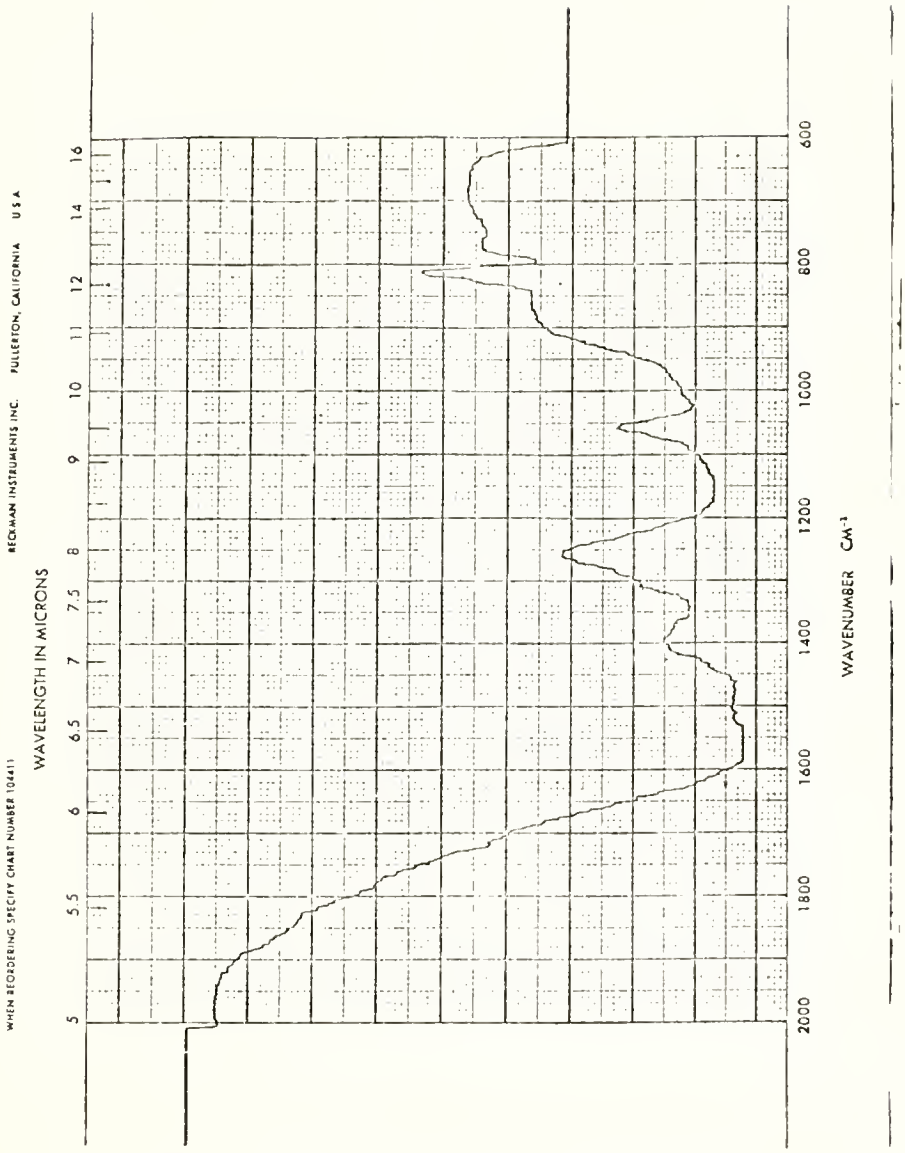

Figure 66. Infrared Spectrum - Admixture Q

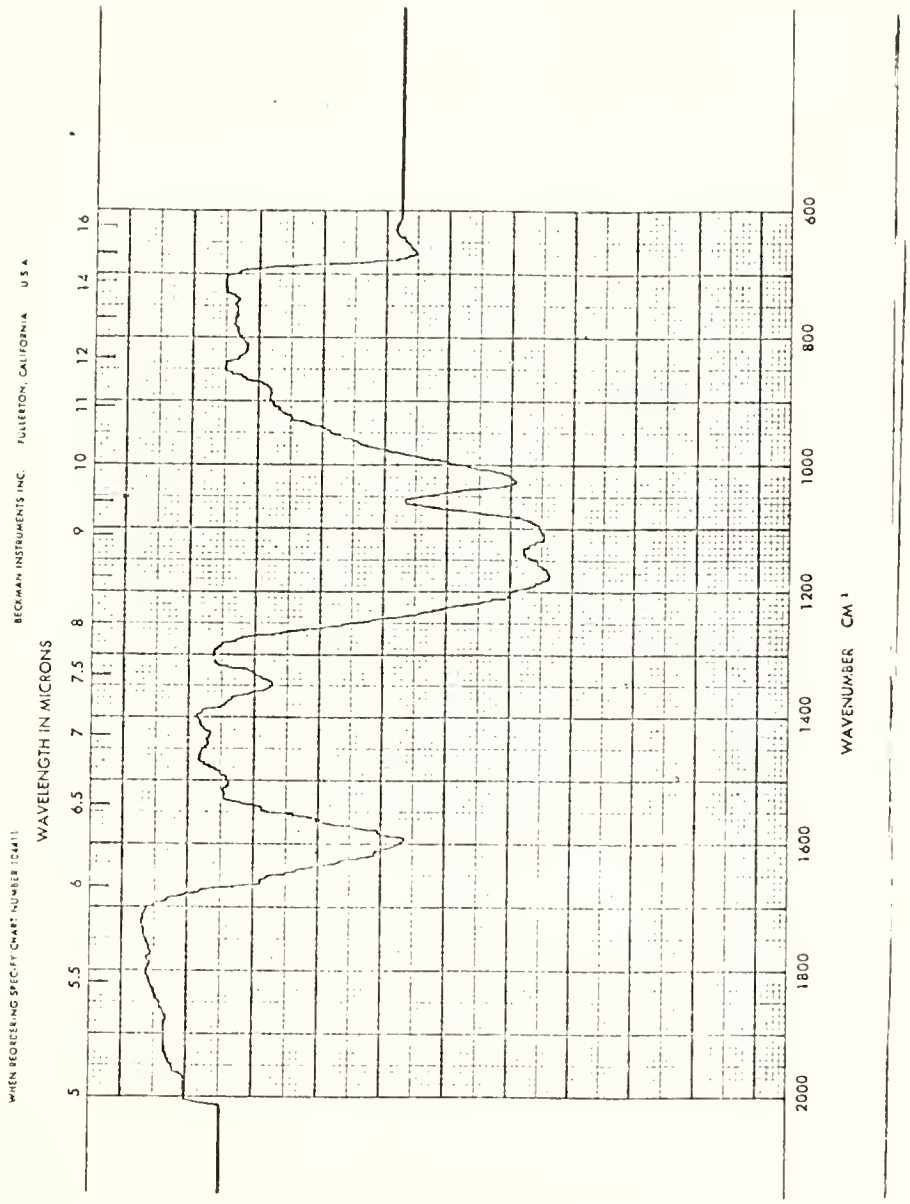

Figure 67. Infrared Spectrum - Admixture R

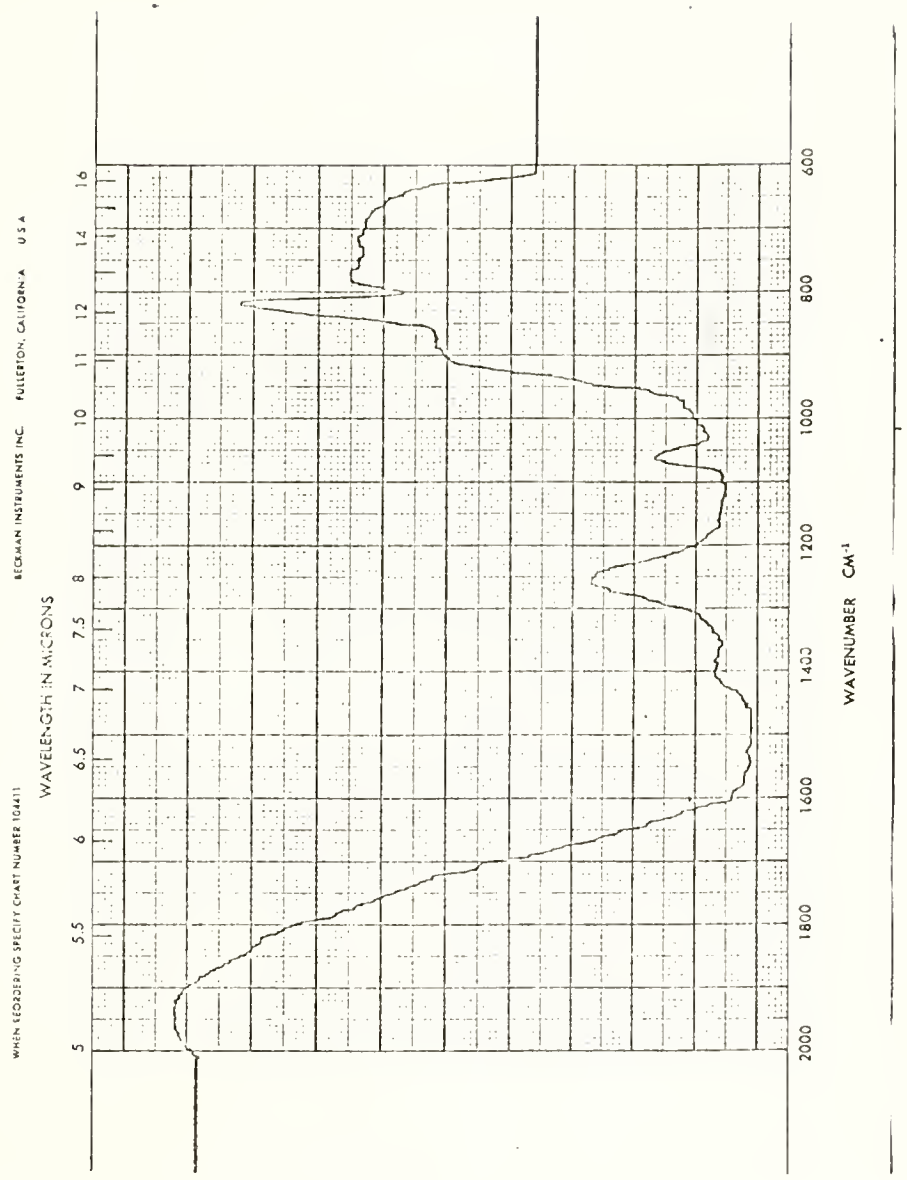

Figure 68. Infrared Spectrum - Admixture S

APPENDIX B

APPENDIX B

Reproducibility of Selected Samples

Figs. 69 through 73 show chromatograms of reruns of some of the dual-sample mixtures, i.e. air-entraining agents together with other admixtures. These were duplicate runs, using the original cement paste samples and the same conditions of extraction and chromatograph operations. A comparison of these traces with their counterparts (Fig. 69 and 41, 70 and 37, 71 and 43, 72 and 42, 73 and 46) shows the reproducibility of the technique.

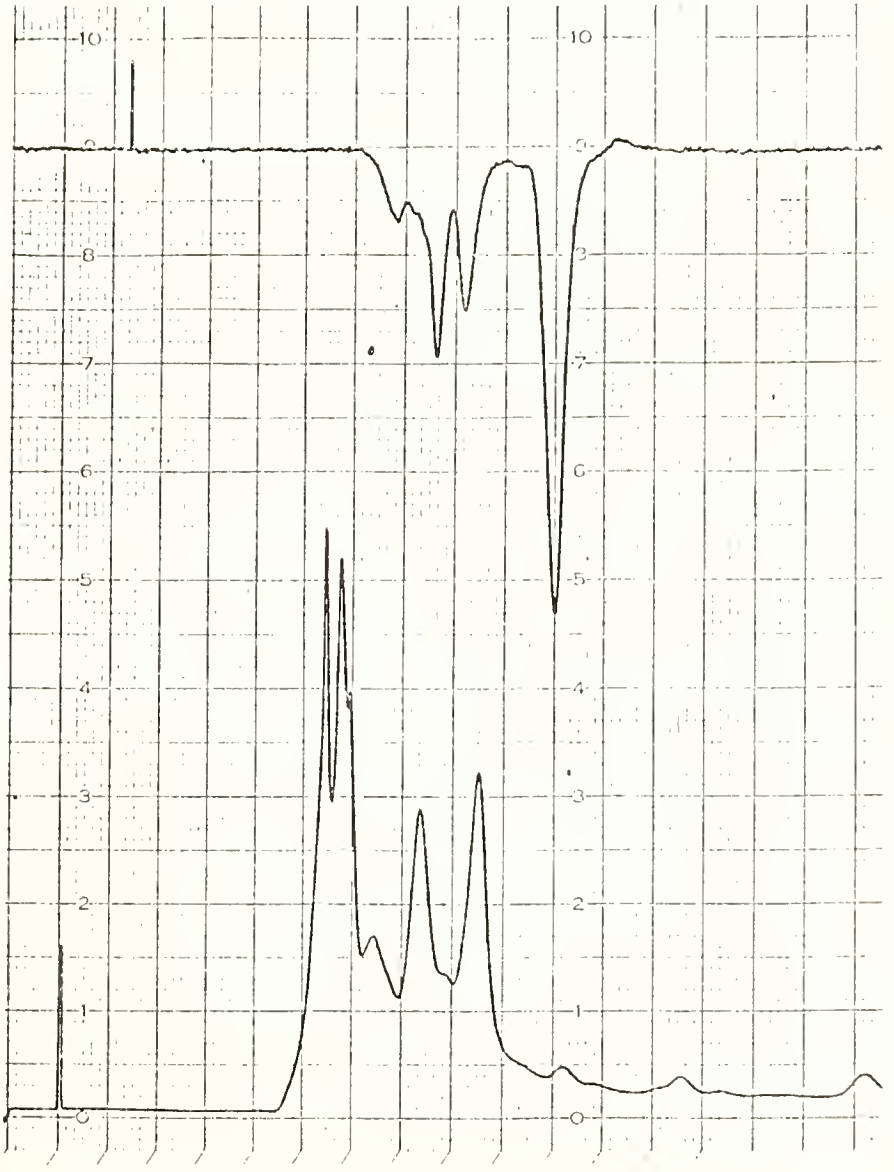

Figure 69. Admixture A-C Rerun

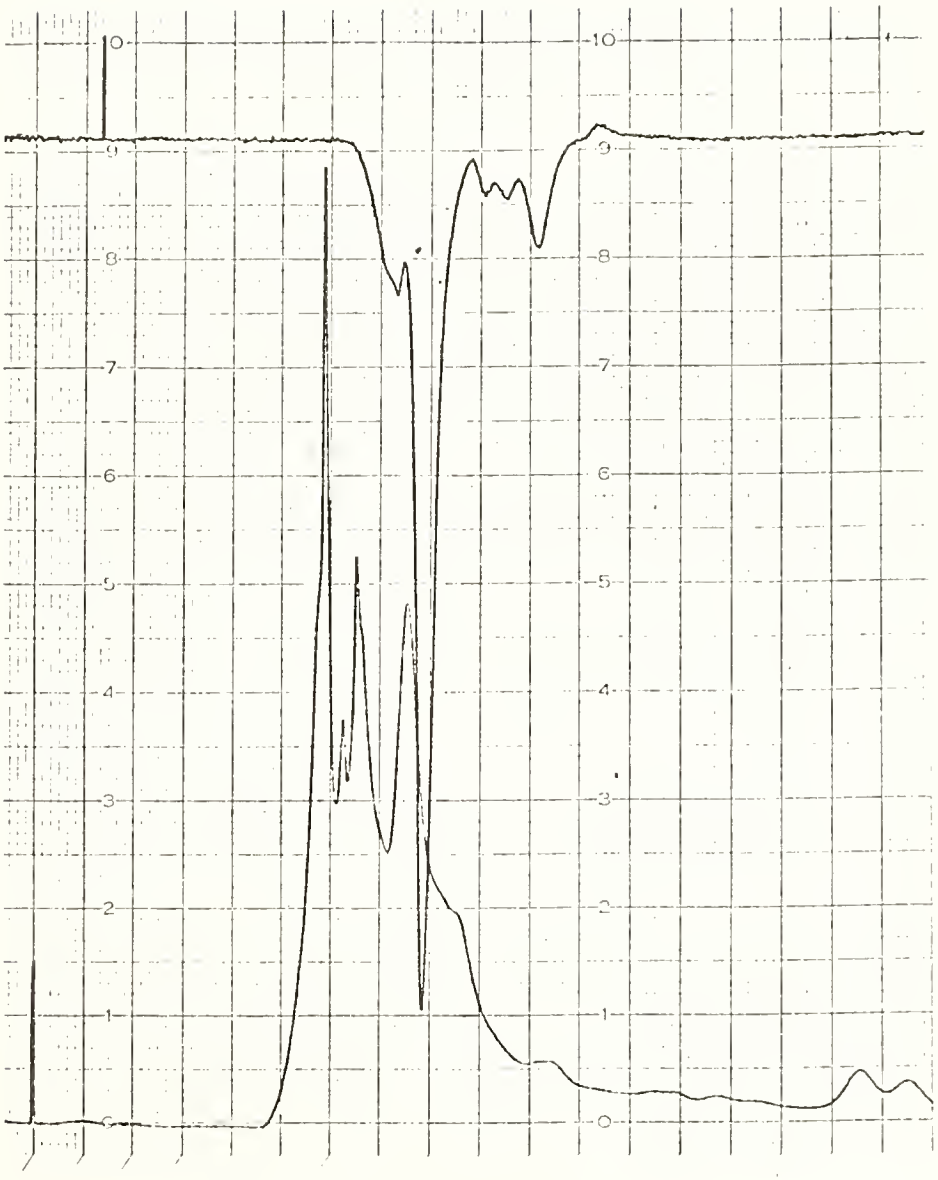

Figure 70. Admixture D-F Rerun

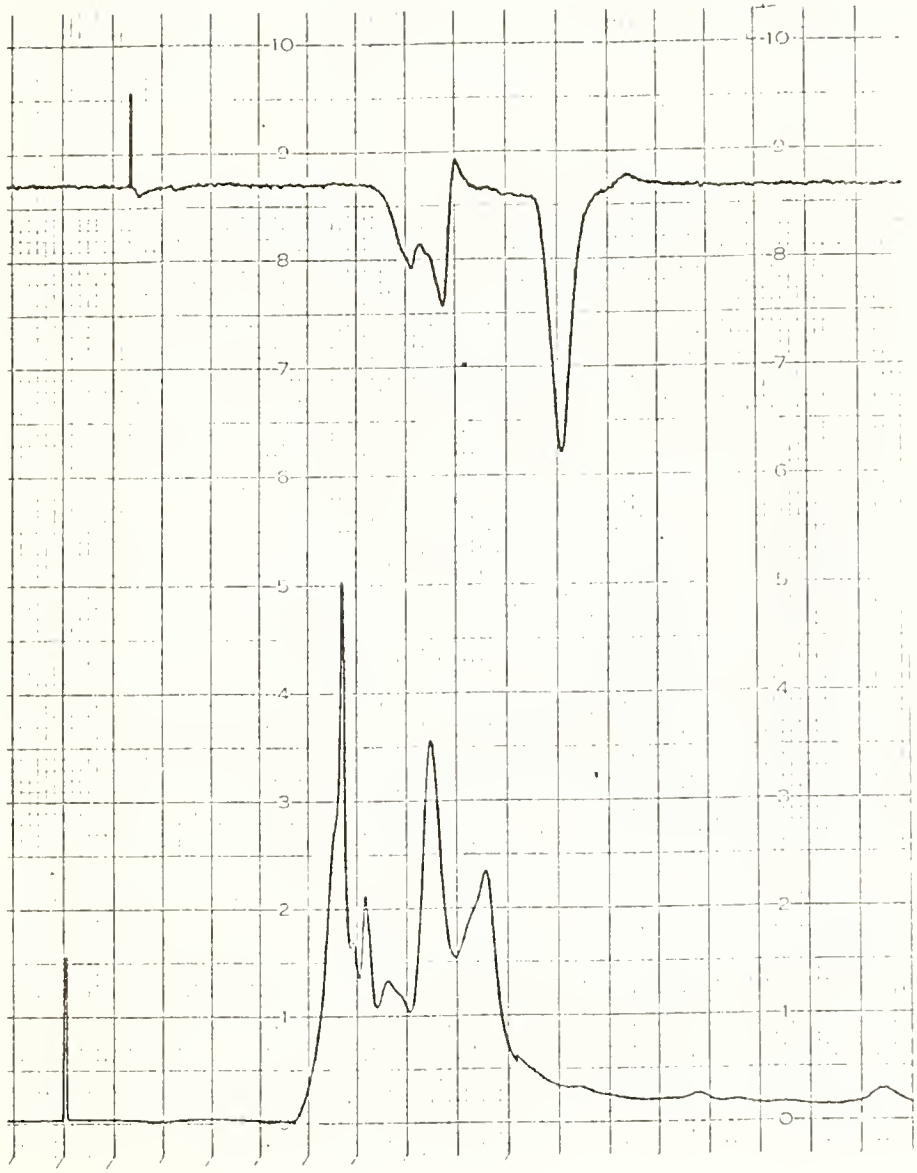

Figure 71. Admixture D-G Rerun

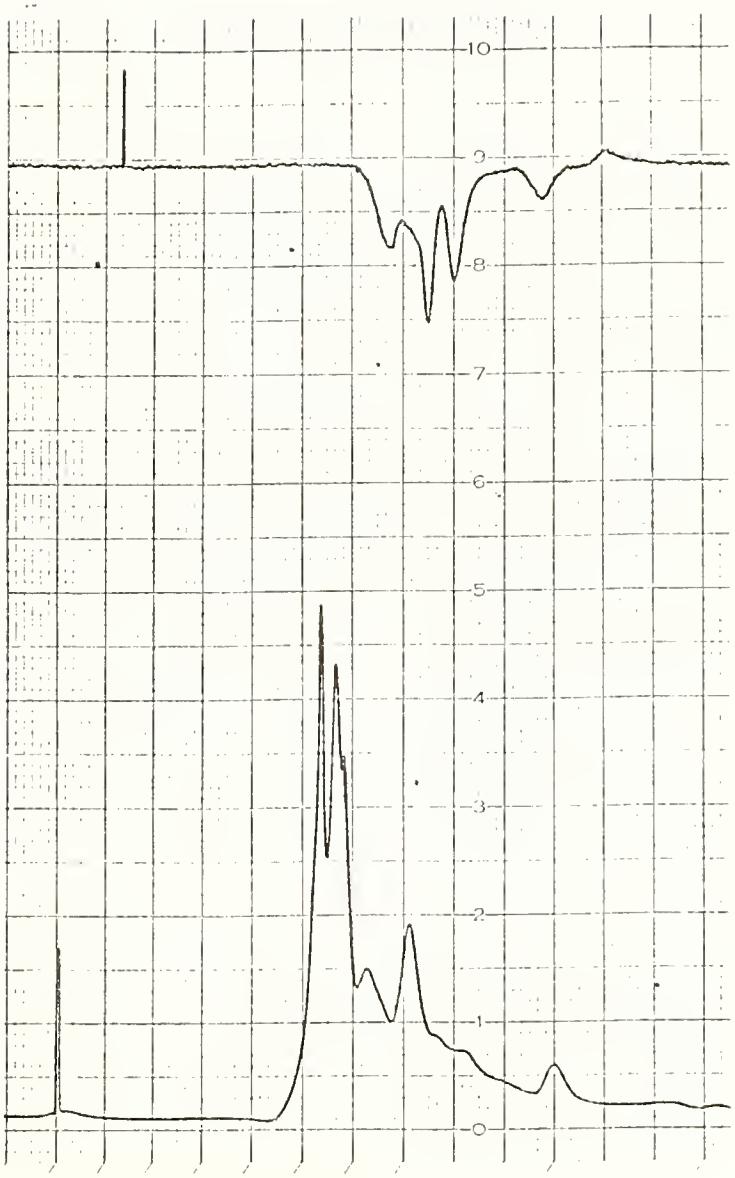

Figure 72. Admixture K-0 Rerun

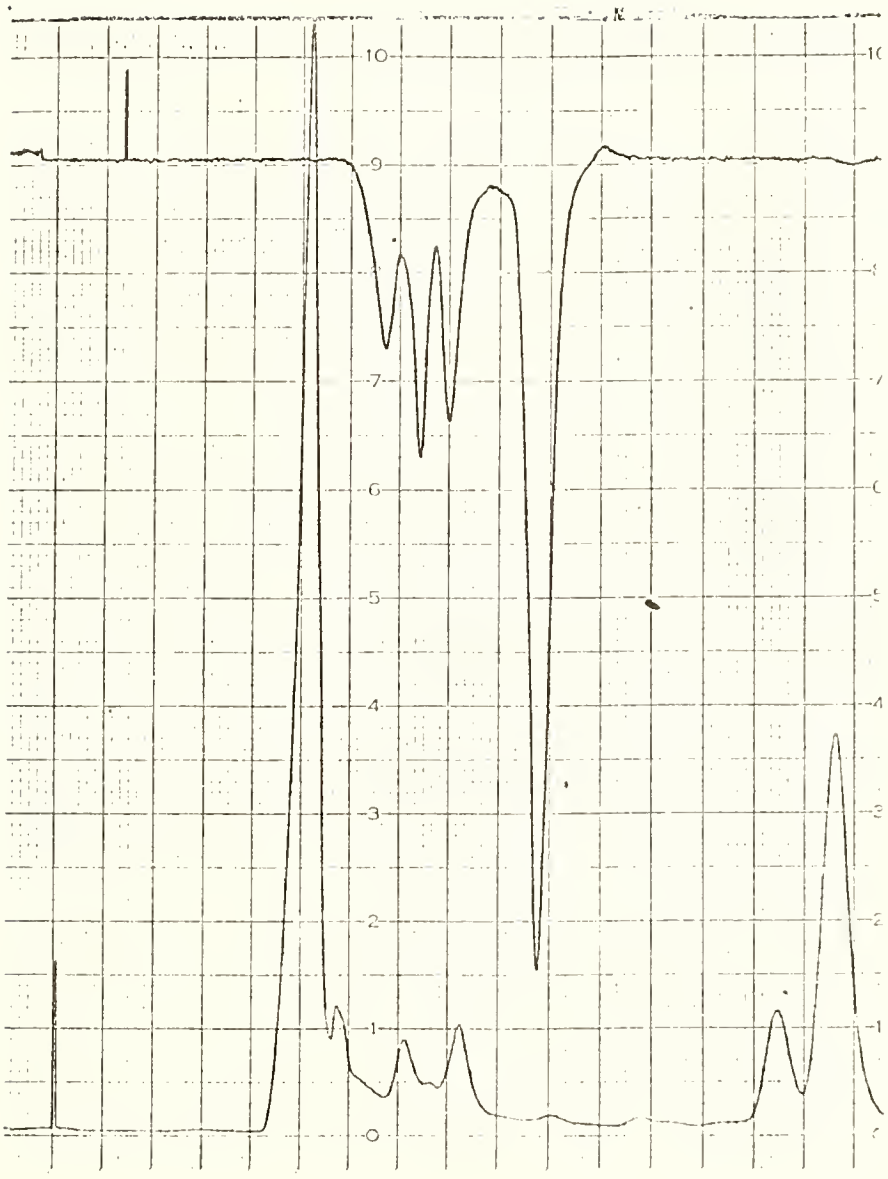

Figure 73. Admixture K-P Rerun

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